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The opinions expressed by the authors are their own and do not necessarily reflect the views of the Planning and Development Division of the Fertilizer Corporation of India Ltd.





Nehru at the Inauguration of  
the Sindri Unit of FCI Ltd.  
on March 2, 1952

## *In Memoriam*

JAWAHARLAL NEHRU, one of the main architects of the country's freedom and the maker of modern India, passed away on May 27, 1964. A restless spirit has thus been stilled by the inexorable law that makes death the ultimate end of life. He was much more than the Prime Minister of this country, since it achieved freedom in 1947. He was the undisputed leader of the Nation.

Born on November 14, 1889, and educated at home in his childhood, Jawaharlal Nehru went to Harrow at the age of 15 and in 1910 took the Natural Science Tripos in chemistry, geology and botany from Cambridge. Called to the Bar in 1912, he returned to India in the same year and started practising in law in the Allahabad High Court. From the same year began his unbroken political career in the Indian National Congress, although for some time he was also connected with the Home Rule League started by Mrs. Annie Besant.

In Jawaharlal's sensitive and creative mind, the following influences contributed to the evolution of his economic ideas: academic studies in science, early studies in Marxist philosophy and British Fabian thought, Russian Revolution and his first trip to Moscow in 1927 where he saw for himself economic planning just started on a national scale, and the problem of Indian poverty. These affected his views profoundly and convinced him of the need for socialism in India.

His interest in planning as a means of effecting social and economic changes needed for moving towards socialism came next in the evolution of his economic philosophy. When at the initiative of the then President of the Indian National Congress, Subhas Chandra Bose, the National Planning Committee was set up in 1938, Jawaharlal was rightly chosen its Chairman. In this Committee, he had a foretaste of some of the practical problems of social transformation, which ultimately enabled him, on becoming the Prime Minister, to set up the Planning Commission in 1950 and be associated with it as its Chairman.

He welcomed the revolutionary impact of science and technology and sought to harness these forces to remove the burden of poverty, hunger, squalor and mental stagnation from the lives of his countrymen. His dynamic and all-pervasive leadership included his close association with the scientific efforts of this country as the Chairman of the Council of Scientific and Industrial Research, Chairman of the Atomic Energy Commission, etc. He was the moving spirit behind the annual conferences of the Indian Science Congress, where his inaugural speeches used to be heard with rapt attention.

# Some Structural Features of Carbonaceous Materials with Particular Reference to Graphite and Coal

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Carbonaceous materials like diamond, graphite and coal have been in use for over a hundred years, but their structure, particularly of coal, has been very elusive. In this aspect, technique and practice have advanced ahead of fundamental knowledge. However, there is now a growing interest among the scientists to unravel their constitution as well as their inter-relation to each other. In this paper, the work on the constitution of the above carbonaceous materials by x-ray and other physical methods, like magnetic susceptibility, has been reviewed.

## Introduction

In the realm of carbonaceous materials, there are two broad classifications viz. crystalline and amorphous carbon. Much of the present knowledge on the diverse forms of carbon has been acquired from x-ray studies in conjunction with other physical and chemical studies. However, in the case of amorphous carbon, the formulation of a structural theory, which gives an unequivocal integrated explanation of all the properties of the substances, is far from an achievement. Nevertheless, the structural configuration of many carbonaceous materials show many analogies with those of crystalline graphite, which is the most highly ordered state of a carbon polymer. Besides graphite, the other crystalline form is diamond, which differs from graphite in the structural configuration of carbon atoms. Thus, from the purely theoretical point of view, it is of interest to know how the structures of the various carbon compounds are related to those of diamond and graphite.

## Structural Nature of Crystalline Carbon

Crystalline carbons constitute a special class of carbons. In diamond, there is tetrahedral symmetry, each carbon atom being tetrahedrally attached to four others by single bonds, thus building up large three-dimensional molecules. The diamond crystallises in regular octahedron with characteristic triangular impressions on the octahedral faces. Further, the distance between the carbon atoms varies between 1.54465 and 1.54443 Å in the different diamonds investigated so far.

But the structure of graphite is somewhat different. In this case the carbon atoms no longer have tetrahedral symmetry, and the bonds between them are not single, nor however can they be double bonds, for each carbon atom is linked up with three others to form a plane hexagonal network. Consequently the order of each bond must be  $4/3$ . It is to be noted, however, that diamond can be converted into graphite, but the reverse process was not possible till very recently, when Hall<sup>1</sup> synthesized diamond from graphite in a specially designed apparatus maintained continuously at 200,000 atm. pressure and above 5,000°C.

Graphite consists of hexagonal sheets of atoms piled together to form a layer structure having a perfect basal cleavage, with very weak forces between the layers. Within these planes, the C—C distances are all equal (1.421 Å) and substantially the same as the C—C separation (1.39 Å) in the benzene ring. The layers themselves are 3.3541 Å apart (at 15°C). Obviously the forces operating between basal planes are very different from and far weaker than the bonds within the carbon planes; this is associated with the pronounced cleavage and flaky nature of graphite. The familiar form of graphite has an elongated hexagonal unit with  $a_0 = 2.456$  Å,  $c_0 = 6.696$  Å. It is worthwhile to note here that a well-crystallized graphite may contain only a few per cent of the rhombohedral variety<sup>2</sup>.

The consecutive layers of atoms in graphite do not lie vertically over one another. A majority of graphites (Fig. 1) consists of alternate-layers such as A, B, A,

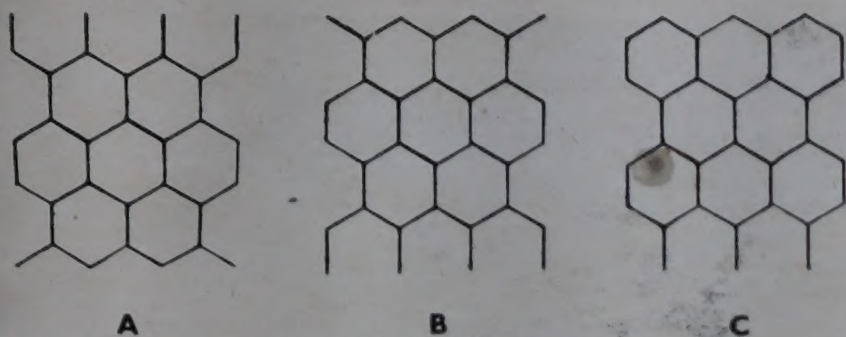


Fig. 1. Structure of Graphite

B;... but some take the form A, B, C; A, B, C;... as well while a small percentage consists of layers randomly arranged. The AB form corresponds to hexagonal variety and ABC form corresponds to rhombohedral variety of graphite with  $A_0 = 3.635 \text{ \AA}$  and  $\alpha = 39^\circ 30'$ .

The curious thing is that natural graphites from different parts of the world, and even artificial graphites, seem to have a fairly uniform 80 per cent of the hexagonal structure and 14 per cent of the rhombohedral structure. Any carbon having an interlayer spacing greater than  $3.3538 \text{ \AA}$  ( $15^\circ\text{C}$ ) is said to contain less than 100 per cent graphite structure—the relation between the two structures being given by Franklin<sup>3</sup> and Bacon<sup>4</sup>. The non-graphitic structure, termed as 'turbostatic' by Biscoe and Warren<sup>5</sup>, refers to that material which shows two-dimensional, but not three-dimensional, ordering by virtue of random rotation of layer planes.

### Amorphous Carbons

The diverse forms of so-called 'amorphous' carbons are in general neither truly amorphous nor truly crystalline, but have structures intermediate between these extremes. They are, in fact, essentially disordered microcrystalline graphites<sup>6</sup>. In this context, it is however to be noted that Warren's work<sup>7</sup> on the structure of amorphous carbons, particularly on carbon black, has opened a new landmark in the structural realm of mesomorphic carbons.

The disordered microcrystalline graphites are distributed at random and in parallel orientation in carbon blacks. The results of Houska and Warren<sup>8</sup> on graphitisation of carbon black have indicated that there is a random orientation of parallel layers about their normal until significant growth of layers occurs to about  $100 \text{ \AA}$  diameter. X-ray and electron microscopic studies by Akamatu<sup>9</sup> et. al. reveal that average particle size of carbon black varies from  $150$  to  $400 \text{ \AA}$ , and in the process of graphitisation by heat treatment they split it into smaller crystallised units. Austin's<sup>10</sup> studies

on a good number of carbon blacks show that the number of stacking parallel layers is between 3 and 4 and the mean interlayer spacing is essentially  $3.52 \pm 0.02 \text{ \AA}$ . The percentage of disorganised carbon of parallel graphitic and non-graphitic layers in carbon blacks depends upon the method of their preparation.

Further researches on above lines have been pursued by a host of workers<sup>11-13</sup>. A number of workers have attempted to trace the changes in the aggregational state of carbonaceous materials from the point of view of pseudo-graphitic nature of amorphous carbons by using x-ray methods. Obviously, the research in coal was mainly directed in relation to the concept of graphite as consisting of fused aromatic rings packed in layers. It is worthwhile to mention here that coal has a heterogeneous structure, and closer chemical and petrographic analyses reveal that it consists of several macerals, like vitrinite, clarainite, fusinite, exinite and micrinite, etc., their structure, chemical constitution, and phase transition in the process of metamorphism of coal are themselves important branches of coal science.

All these 'amorphous' carbons are not pure carbons because they are constitutionally being contaminated with elements like oxygen, hydrogen, nitrogen, etc., in their structural framework. The presence of groups

like  $\text{C}=\text{O}$ ,  $\equiv\text{CH}$ ,  $-\text{COOH}$ , etc., has been found in

them. The general objective of such studies was to determine the structural properties of the substance for possible correlation with other data, such as hydrogen and oxygen contents. The ultimate aim is to find the size of carbon layers, extent of stacking into parallel layers, and the amount of disorganized carbons. X-ray methods have provided some of the most precise data on all these aspects.

Again, most carbonaceous solids are porous, their porosity may be due to capillaries covering a wide range of sizes from a few angstrom ( $\text{\AA}$ ) units to many microns in width. It is the presence of capillaries of the order of molecular size (i.e. ultrafine), which is responsible for the behaviour of many such materials.

### COAL

The last four decades have seen a growing interest in x-ray scattering studies on coal. The first of its kind was made by Mahadevan<sup>14</sup> on Indian coals, who observed two diffuse haloes at  $3.31$  and  $2.21 \text{ \AA}$  corresponding to the two strong lines of graphite. This led him to believe that coal consists of submicroscopic graphitic layers. Further, it is observed that there is no band in

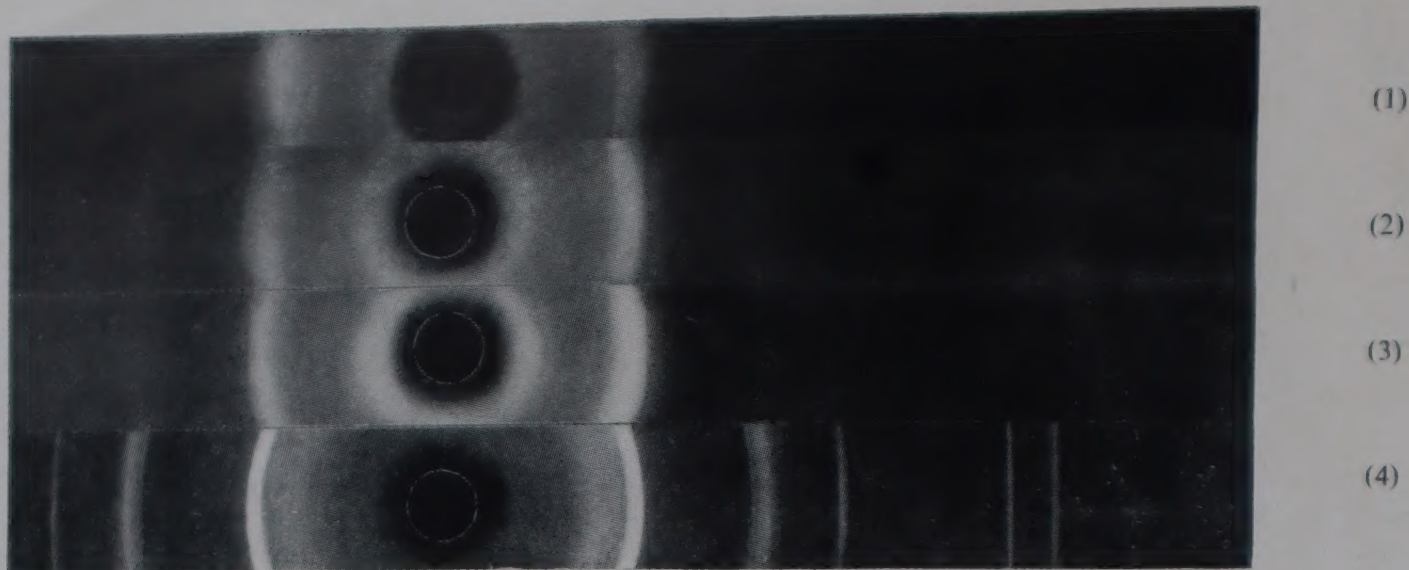


Fig. 2A. X-ray Diffraction of Photographs of Coal  
[(1), (2) & (3) Coals in Increasing Order of Carbon Content; (4) Ceylon Graphite]

x-ray picture of coal corresponding to the oblique reflection planes, like (103), (112), etc. of graphite crystals.

After Mahadevan's observations, several workers in different parts of the world were interested in x-ray studies on coal. Their studies can conveniently be divided into three parts—low, medium and high angle regions. The object was to determine its pore system, the average diameter of small sheets of graphite and the number of sheets per group.

Much of the earlier work was done on medium and high angle regions only. Riley<sup>11</sup> and others obtained two or more diffuse bands at the positions of the strong lines of graphite, and as coalification proceeded the bands became more prominent as shown in Fig. 2A obtained by the author. They suggested that the two dimensional, graphitic type, aromatic planar rings are distributed at random in low rank coals and those rings become more and more parallel during coalification to higher ranks. Nelson<sup>15</sup> found that the position of (002) of band is progressively changed with the carbon content and the d spacing value extrapolated to 100 per cent carbon coincides with the d-value of graphite. This evidence, he states, gives strong support to the existence of aromatic rings.

In their study of low angle region of coal, Brusset<sup>16</sup> et al found that the scattered intensity continuously increased with decreasing angle. They explained this to be due to nearly spherical micelles of diameters between 40 and 200 Å which are believed to consist of molecules of aromatic ring clusters surrounded by carbonaceous materials of different electron density. Riley's<sup>17</sup> studies have led to the observation of a well-defined band of about 25-28 Å spacing due to closely packed spherical

particles of diameter 30-35 Å. Nelson and Hirsch also observed the 20 Å band, and Hirsch interpreted this to be due to ordering of aromatic layers of 2 to 3 at about 20 Å to one another. They explained the continuous scattering at very small angle regions to be due to differing electron densities of continuous phase and to the sub-microscopic pores some of which are anisotropic and disc-like in shape.

In this context, it is necessary to include a brief discussion on the pyrolysis of coal. During pyrolysis coal remains unaffected up to 300°C; from 300°C to about 550°–650°C, its decomposition to semi-coke takes place with the emission of volatile matter and gases. At about 650° to over 1000°C, transformation of semi-coke takes place with the emission of volatile matter and gases. The carbonization process is divided as follows:—

Semi-carbonization	about 400°–650°C.
Carbonization	about 650°–1000°C.
Semi-graphitization	about 1000°–1400°C.
Graphitization	about 1400°–2300°C.
Crystallization	about 2300°C

The chemical and physical changes occurring during pyrolysis are exceedingly complex. In general, carbonization is accompanied by aromatization (Fig. 2B). Further, the properties of the carbonized products are determined by the rate of heating and the highest temperature reached. Some interesting results of x-ray study on cokes have been reported, wherein it is observed that the layer diameter and the number of layers per group are determined by the temperature of carbonization and the rank of coal as shown below (Table 1).



Fig. 2B. X-ray Diffraction Photograph in Increasing Order of Carbonization Temperature  
[Cu K $\alpha$  Radiation; Camera Diameter 5.73 cm.].

TABLE 1—X-RAY STUDY OF COKES (AFTER FRANKLIN<sup>12</sup>)

Sp. No.	Parent Coal	Layer diameter, Å	Number of layers per group	Temperature, °C
1.	Welsh Anthracite (94.3% C)	30 50 80	4.1 7.2 13.7	1,460 2,070 2,290
2.	Welsh Anthracite (93.9% C)	35 85	5.0 13.5	1,460 2,290
3.	Welsh Coking Coal	40	12	1,460
4.	Yorkshire Coal (83.1% C)	57	10	2,850
5.	Northumberland Coal. (82.4% C)	47 65	7.4 11.6	2,160 3,000

Again, in some coals there is an additional band with spacing around 4.35 Å inside the (002) reflection and this band is usually known as  $\gamma$ -band.<sup>11-16</sup> The origin of  $\gamma$ -band has been attributed to the presence of exinite in vitrain. It is to be noted, however, that all these materials—the ultimate fractions of coal—such as vitrinite, fusinite, exinite and micrinite differ from each other in physical behaviour and chemical composition. However, there are some generalisations regarding their composition and constitution. Fusinite

is usually rich in carbon content and low in hydrogen content when compared with the vitrain of the same coal. With change in rank, fusain shows only little differences in carbon and hydrogen contents, while in the case of vitrain there are wide compositional differences with rank.

Till now, the experimental data were interpreted assuming that the coal consists of fused aromatic ring clusters. But Warren<sup>7</sup> suggested that structural information should better be obtained by calculating the atomic distribution functions without any previous assumptions. He developed the theory of diffraction for random layer lattices. Using this theory Hirsch<sup>13</sup> calculated bond lengths, size of the layers and percentage of carbon in each, and found that the layer diameters varied from 7 to 9 Å for vitrains of 78 to 89 per cent carbon, and the layer diameters increased rapidly with more carbon content. He calculated the crystalline portions to be about 65 to 80 per cent. He developed the Fourier Inversion technique for the medium angle region and showed that the layers occur partly in single and partly in two, three or more stacked parallel to each other.

As Warren's treatment of random layer structures yielded not very satisfactory results, Cartz<sup>18</sup> et al later developed a matrix method based on the principle of least squares for the Debye-radial distribution functions for the various molecular size groups of layers. He computed theoretically the scattered intensity for the layer

diameters of 5.8 to 20 Å, and compared the results with the experimental data. Taking into account the effect of hydrogen and oxygen atoms, probably occurring as OH and CH<sub>2</sub> groups, on the peripheral sides of the aromatic layers, elongated molecules and holes in the molecules, he concluded that the amorphous forms, including CH<sub>2</sub> and OH groups, get reduced in proportion by carbonization at higher temperatures, and the aromatic layers get packed better. The rate of growth is approximately linear up to 1000°C.

The rate of growth is greater for anthracites probably because comparatively the large layers are better aligned in the initial stage itself. The average bond-length after initial reduction increased gradually with temperatures in accordance with the growth of layers. The growth of layers is accompanied by the appearance of a large-scale porosity.

In spite of so much work on coal, its structure is yet to be known precisely. From x-ray studies it could only be concluded that coal is constituted of cross-linked and parallel layers of aromatic rings and the number of aromatic rings is small up to 90 per cent carbon, probably between 2 and 4, and contains a large amount of smallest layers and amorphous carbon. It is yet to be decided whether there are single benzene rings, five-membered rings, or aliphatic and alicyclic chains, etc., and whether these rings or chains are attached to the layers or they exist independently.

Nevertheless, there has been a growing interest to unravel the structure of coal in spite of its complex structure. One of the simplest models has been shown in Fig. 3 (after Van Krevelen). This is to be treated as the statistical average of a number of possible units

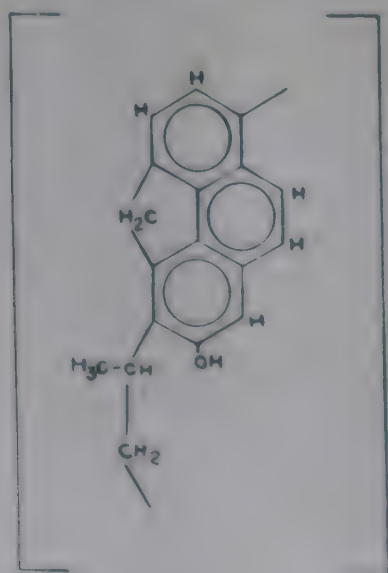


Fig. 3. Simplest Model of Structural Unit  
[C<sub>11</sub>H<sub>11</sub>O]<sub>n</sub> in Coal Vitrinite 83%]

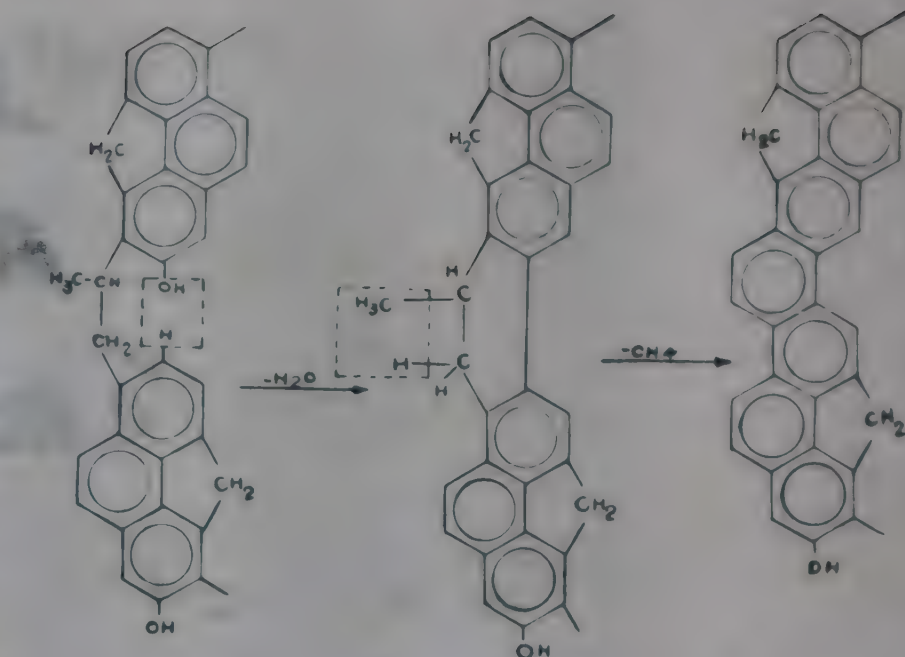


Fig. 4. Simplest Mechanism of Coalification  
[From Carbon Content of about 83 to about 93%]

in a polymeric structure. This model is in agreement with quite a number of experimental facts.

Alicyclic rings are not shown in this model but can be found on proceeding to the higher ranks of coal (Fig. 4).

## DISORDERED GRAPHITE

So far the concept of pseudographite structure has been sponsored for the elucidation of the structure of the amorphous carbons. Keeping this in view, it would be interesting to know some salient features of degraded graphite structure.

The degradation of the structure of graphite occurs under neutron bombardment in nuclear reactors and also by mechanical grinding. The extent of damage can, however, be estimated by the critical analysis of the x-ray picture with particular reference to the line broadening of some selective planes of graphite. The crystallite sizes and d spacing of graphite do vary appreciably with the duration of irradiation and the intensity of grinding. On grinding graphite, the layer planes are actually broken up, which destroy the order in the stacking. As a matter of fact, with more intense grinding, crystallite dimensions (both layer plane and layers per group) become reduced causing a general deterioration in the degree of crystalline perfection. Some interesting accounts to this end have been reported.<sup>20,21</sup>

Curiously enough the general physical characteristics of these finely divided graphite particles show a strong parallelism with those of many pseudo-graphitic carbonaceous materials like coal, as is evident from the comparative study of the following two tables (Tables 2 & 3).

TABLE 2—CRYSTALLITE DIMENSIONS OF FINELY DIVIDED GRAPHITES (WALKER AND SEELEY<sup>21</sup>)

Sample	Crystallite Thickness, Å	Crystallite diameter, Å	d-spacing, Å
3 $\mu$	>1000	>1000	3.354
1	172	416	3.356
2	122	280	3.362
3	9		3.78
4	9		3.81
5	8		3.87
6	8		3.84
7	9		3.80

TABLE 3—CRYSTALLITE DIMENSIONS OF VITRINITES (HIRSCH<sup>13</sup>)

C on dmmf basis, %	Maximum layers per crystallite	Layer diameter, Å	Interlayer distance, Å
94.1	8—10	16	3.43
91.4	8	11	3.52
89.3	7—8	9	3.50
89.0	7—8	9	3.52
87.3	6	7	3.52
84.4	5—6	8	3.54
80.1	4—5	8	3.64
78.3	3—4	7	3.75

### Electrical & Magnetic Properties of Carbon, Graphite, Coal, Etc.

The electrical and magnetic properties of mesomorphous carbons show many analogies with those of the crystalline graphite. The electrical conductivity of a single crystal graphite has been studied by a number of workers.<sup>22-26</sup> The conductivity of a graphite single crystal along with direction perpendicular to the hexagonal axis is about  $10^4$  times than that along the axis. Again, the conductivity perpendicular to the hexagonal axis falls roughly exponentially with rising temperature and that along the axis rises similarly with temperature. Some amorphous carbons like anthracite coal, carbonized coal, etc., have measurable conductivity with temperature dependence similar to that of conventional intrinsic semi-conductors, though the absolute value of conductivity is several orders of magnitude lower than in most semi-conductors.<sup>27, 28</sup>

It is well known that crystalline graphite exhibits large diamagnetic anisotropy.<sup>29</sup> The susceptibility value perpendicular to the hexagonal axis is small and similar to that of diamond ( $-0.5 \times 10^{-6}$  C.G.S. units/g), while

the susceptibility value along the hexagonal axis is nearly forty-four times greater (i.e. equal to  $-21.5 \times 10^{-6}$  C.G.S. units/g). The large anisotropic component of the susceptibility is, moreover, distinctly temperature-sensitive and shows a negative temperature dependence. Some interesting accounts of the finely divided particles of graphite have been reported,<sup>30</sup> where it is shown that the susceptibility along the hexagonal axis diminishes to about  $-0.9 \times 10^{-6}$  C.G.S. units/g, in particles of less than 2 microns diameter.

The diamagnetic susceptibility<sup>31</sup> of coal lies around  $-0.5 \times 10^{-6}$  to  $-0.6 \times 10^{-6}$  C.G.S. units/g. There have been several studies of the magnetic changes which occur in carbon during graphitization and also during the process of carbonization from a variety of carbonaceous materials. There is an intimate relation between the crystallite diameter and the diamagnetic susceptibility value.<sup>32, 33</sup> It is usually observed that polycrystalline graphite, coal, coal extracts, carbon black and carbons formed by pyrolysis of various organic materials, exhibit diamagnetism in varying magnitude.

Further, it is reported that coal contains a paramagnetic part and this paramagnetism is due to the unpaired electron linked with the organic structure of coal. Paramagnetic resonance studies of coal and coke have revealed some interesting results.<sup>34-37</sup> Studies on coal reveal a steep rise in radical concentration between 80 and 94 per cent carbon content. The number of free radicals found in coal was of the order  $1-3 \times 10^{19}$ /g. As the carbon content rises above 94 per cent, an extremely sharp fall takes place. Similarly in the carbonization process, the free radical concentration is seen to rise to a maximum when the carbonization temperature is raised through  $550^\circ\text{C}$  and then falls abruptly.

### Acknowledgements

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# Stress Corrosion Cracking of Metals

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Some general aspects of the phenomenon of stress-corrosion cracking of metals have been described. Among the topics discussed are: creation of stress in metallic equipment, electro-chemical theory of corrosion, theories for the mechanism of stress-corrosion cracking and remedial measures against this type of failure.

## Introduction

The so-called 'season cracking' of brass, as it was known in the nineteenth century, is the earliest example of stress-corrosion cracking. Although initially the cause of the failure was not known, the cracking has subsequently been shown to be due to the action of ammonia in the atmosphere on stressed brass. The first recorded experiment on stress-corrosion cracking was performed by Roberts-Austen who showed that a hard-drawn bar of gold-copper-silver alloy (Au 54.17, Cu 33.13, Ag 12.53 per cent) would crack within a short time if moistened with a solution of ferric chloride.<sup>1</sup> Later on, it has been shown that most of the metallic elements make some alloys which are liable to failure

by stress corrosion.<sup>2</sup> Even some materials which were formerly thought immune to this form of corrosion have now been known to undergo cracking in special environments, e.g. monel in aerated hydrofluoric acid vapour<sup>3</sup>, titanium in red fuming nitric acid.<sup>4</sup> However, in practice stress-corrosion cracking appears to be a major cause of failure only with relatively few types of alloys, notably brasses, some aluminium and magnesium alloys, carbon steel and austenitic stainless steels. Examples of such failures are stress-corrosion cracking of copper-zinc alloys (brasses) in ammoniacal media, of aluminium alloys (containing 5-9 per cent magnesium) in aqueous solutions containing chlorides, of magnesium alloys in sea-shore atmosphere, of carbon

steel in nitrates, alkalies and humid hydrogen sulphide and of austenitic stainless steel in solutions containing chlorides, alkalies and nitrates.

There is a lack of universally accepted definition of stress corrosion. Uhlig has made a distinction between two terms: stress corrosion and stress-corrosion cracking.<sup>5</sup> Stress corrosion is defined as the combined effect of stress and corrosion on the behaviour of metals, and by stress-corrosion cracking is meant the cumulative action of static stress and corrosion which leads to cracking of metals.

Stress, however, has no more than a minor effect on the rate of general corrosion, and, as pointed out by Champion, the following single definition of stress corrosion, which is accepted in the U.K., is adequate<sup>6</sup>: "The term 'Stress-corrosion' implies a greater deterioration in the mechanical properties of the material through the simultaneous action of a static stress and exposure to corrosive environments than would occur by the separate, but additive, action of these agencies." Such factors as corrosion fatigue and corrosion due to diffusion of liquid metals are excluded from the definition of stress corrosion.

The subject of stress-corrosion cracking in metals has been studied extensively by many investigators. It is not possible to give a survey of the work done in the field due to limitations of space; only some general aspects of the subject will be considered in this article.

### Origin of Stress in Metallic Equipment

Stress corrosion failures usually take place under the influence of high residual tensile stresses. Applied loads add up to these stresses, but, by themselves, are not of much significance since they are usually small in comparison with residual stresses. However, in pressure vessels and in deep oil wells, applied loads have a significant role in stress-corrosion cracking.

Residual stress in metals may arise from differential volume changes resulting from unequal cooling, from precipitation of a new phase, from transformation reactions and from heterogeneous shape changes. They are also produced in an assembly by press-and-shrink fits, welding and rivetting.

Many of the changes described above take place during manufacturing operations involving cold deformation i.e. deformation of metals well below the recrystallization temperature. As a result of this deformation, the random-oriented grains of a polycrystalline material first become oriented in a preferential direction and the grains are displaced with respect to

each other. With increasing deformation, the crystallite finally breaks up into new grains. The deformation is also accompanied by phase transformation in many cases e.g. precipitation and coagulation of carbides take place in carbon steel, and in stainless steel the austenite is transformed into martensite and ferrite. These changes in microstructure lead to residual stresses in the metallic equipment.

Since a large number of metallic equipment are made up of welded components, the residual stress left after welding assumes special significance. As the result of heterogeneous temperature distribution during welding and the structural transformations that occur in zones along the weld, where the metal is heated above the critical temperature, large tensile stresses are created in the metal when it is cooled. These stresses are created in the weld zone in the direction parallel to it.

### Electro-Chemical Theory of Corrosion

Corrosion processes are recognised to be electro-chemical in nature. The complete corrosion reaction is divided into an anodic portion and a cathodic one occurring simultaneously at discrete points on the metallic surfaces. The anodic reaction e.g.  $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}$  represents loss of electrons (Oxidation) by the corroding metal, while cathodic reaction e.g.  $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$  or  $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^-$  represents gain in electrons (reduction). The weight of the metal dissolved by the anodic corrosion reaction depends upon the current passing between the anodic and cathodic zones and is given by Faraday's law. The formation of discrete cathodic and anodic zones on a metallic surface is caused by various factors<sup>7</sup> e.g. differential thermal metallurgical treatment, local differences in surface roughness, presence of local scratches, inclusion of different phases, etc.

This electro-chemical theory of corrosion has received experimental confirmation. One strong evidence in support of this theory is the fact that the corrosion of a metal may be prevented in suitable circumstances by cathodic protection. In cathodic protection, arrangement is made for flow of electrons to the corroding metal by keeping it in electrical contact with a more anodic metal or by passing current from an external source through an unattackable anode placed in the solution. By either of these processes the local cathodes in the metal are polarized and their potential approaches that of the local anodes. In order that corrosion may be stopped completely, the current flow between the local anodes and local cathodes should be reduced to zero, and for this purpose conditions should be so

arranged<sup>8</sup> that the local cathodes in the metal are polarized to a potential equal to or more anodic than the local anodes, the latter condition being necessary when cathodic polarization is small compared with the total resistance drop. This process is known as cathodic protection since the protected metal is cathodic towards the external electrode.

### Mechanism of Stress-Corrosion Cracking

In discussing the mechanism of stress-corrosion cracking certain general aspects of this phenomenon should be taken into consideration. It has been found that only tensile stresses cause cracking; compressive stresses have actually been found beneficial. The cracking may be along the grain boundaries (intergranular) or across the grains (transgranular). The same metal may fail by intergranular cracking in one environment and by transgranular cracking in another. Thus, the stress-corrosion cracking of carbon steel has been found to be intergranular in nitrate solutions<sup>9</sup> and transgranular<sup>10</sup> in hydrocyanic acid solution; the cracking of some magnesium<sup>11</sup> alloys has been found to be intergranular in certain environments and transgranular in others.

A generalized mechanism of stress-corrosion cracking applicable to all metal systems would be highly desirable. However, universal agreement has not been reached so far on such a mechanism, although it is recognised that certain broad principles apply to all cases of stress-corrosion cracking. The different theories about the mechanism of stress-corrosion cracking at least recognise that corrosion due to electro-chemical action is one of the factors; the difference lies in whether the important role is assigned to electro-chemical action or to mechanical effect.

In a number of investigations it has been shown that stress-corrosion cracking can be prevented by cathodic protection. Thus, Mears et al<sup>11</sup> showed that stress-corrosion cracking of austenitic stainless steels can be prevented by mild cathodic protection. Priest, Beck and Fontana<sup>12</sup> studied stress corrosion failures of a magnesium base alloy containing 6 per cent aluminium, 1 per cent zinc and 0.2 per cent manganese in a 3 per cent sodium chloride - 3 per cent potassium chromate solution at room temperature. Both intergranular and transgranular cracks were observed depending upon heat treatment and other factors. Motion picture microscopy of the crack initiation and propagation was accomplished. Cathodic protection by means of an external current prevented the initiation of both intergranular and transgranular attack and even stopped the cracking which was in progress. These and

other experiments of a similar nature, which show that cathodic protection prevents stress-corrosion cracking, confirm the role of electro-chemical factor in this type of failure. Priest, Beck and Fontana<sup>12</sup> assign a subordinate role to stress, because they are of the opinion that stress contributes only to the overall electro-chemical mechanism by causing film breakage whereby the local cell action takes place between large filmed areas (cathodes) and extremely small film-free areas (anodes) at the crack tip. Hoar<sup>13-17</sup> et al carried out detailed investigations on stress-corrosion cracking of austenitic stainless steel in boiling magnesium chloride solution and arrived at a mechanism which is essentially electro-chemical in nature. According to this theory, there is an induction period before crack initiation. During this period electro-chemical reactions leading to corrosion takes place but there is substantially no mechanical damage. The anodic regions, at which the metal goes into solution, are grain boundaries, sub-grain boundaries, emergent dislocations, strained zones produced by local quenching stress or cold work or small zones of the martensite that can be formed by cold work. These disarranged regions are activated by stress. Galvanic action between cathodic zones on the surface of the metal and a small stressed disarrayed region (anodic) produces a sharp notch or crack-pit, following the disarrayed region in depth. More recently Hoar<sup>17</sup> has expressed the opinion, based on experimental work by Neilson, that the crack-initiating disarrayed regions are most probably the sub-microscopic corrosion tunnels that are formed at the slip bands. Rapid crack propagation begins when the stress at the advancing edge of a notch reaches a limiting value, probably corresponding to the particular rate of yield of the material. The crack propagates by the continuous anodic dissolution of its highly stressed advancing edge.

Van Rooyen<sup>18</sup> has supported the above mechanism on the basis of his investigations. The existence of an induction period before crack initiation, as proposed by Hoar et al, seems also to be supported by the work of Hawkes, Beck and Fontana.<sup>19</sup> The postulate that crack propagation occurs entirely as a result of an electro-chemical mechanism has been opposed by some workers mainly on the ground that the observed rates of crack propagation seem to be too high to be accounted for simply by a corrosion reaction. The combined action of stress and corrosion mutually "trigger" a deformation process which results in the production of brittle cracks and the process of stress-corrosion cracking is taken to be primarily mechanical. Among those who have supported such a mechanism of stress-corrosion cracking are Keating,<sup>20</sup> Gilbert and Hadden,<sup>21</sup> and Len

and Helle.<sup>22</sup> Farmery and Evans<sup>23</sup> carried out stress-corrosion experiments with aluminium (7%)-magnesium alloy in aluminium chloride solution and with aluminium (4%)-copper alloy in caustic soda solutions. Cracking occurred without the appearance of conspicuous corrosion products and the surfaces were found to be bright. From this the authors conclude that the cracking is mainly mechanical and the role of the electro-chemical action is simply to demolish the obstacles which would otherwise hold up the advance of the crack. The authors, however, recognise that there may be cases where electro-chemical action eats its way along a continuous path across the metal, as in the mechanism proposed by Hoar<sup>13-17</sup> et al for transgranular stress-corrosion cracking of austenitic stainless steel.

An altogether new approach in obtaining an insight into the mechanism of stress-corrosion cracking has been made by Gulbransen.<sup>24</sup> He showed by studies with electron microscope that whiskers of oxides grow on austenitic stainless steel in pure oxygen and water vapour. When a trace of chloride is present, the whiskers change to rows of thin parallel plates which grow along definite crystallographic directions. Each platelet grows to a height of 100,000 Å and to a length of over 250,000 Å. Gulbransen thinks that the tiny canyons left after these growths allow stress concentration at the base which may lead to stress-corrosion failures. Further work along these lines is expected to be of considerable value.

### Avoidance of Stress-Corrosion Failures

In a report prepared by a NACE Committee<sup>22</sup> the various steps recommended for preventing stress-corrosion cracking of austenitic stainless steel were classified broadly under three categories: (1) change material; (2) reduce or eliminate the stress; and (3) change corrosion environment. These recommendations are applicable not only to austenitic stainless steel but to all metals susceptible to stress-corrosion cracking. They are discussed below in detail.

(1) *Changing of Material of Construction:* Changing of material of construction may eliminate stress-corrosion cracking in many cases. Thus, unlike austenitic 18-8 stainless steels, titanium, Hastelloy-F and iron-chromium nickel alloys containing 40 to 65 per cent nickel are immune to stress-corrosion cracking in aqueous solutions containing chlorides. Although these materials are costlier than 18-8 stainless steel, their use may well be justified in some cases to eliminate stress-corrosion cracking. There are instances where stress-corrosion

cracking has been minimised by changing material of construction without appreciable increase in equipment cost. For example, the stress-corrosion cracking of a tubular condenser made of type 304 austenitic stainless steel in chloride containing water was prevented by using type 430 and 446 stainless steel.<sup>23</sup> In another case,<sup>23</sup> cracking of a cooling coil of type 347 stainless steel, through which water at 80°F containing 25-3000 ppm of chloride ion was circulated, was prevented by using a coil of bimetallic tubing with stainless steel on the outside and admiralty brass on the inside.

(2) *Reduction of Stress:* Reduction or elimination of stress, wherever possible, should always be done to prevent stress-corrosion cracking.

The residual stresses remaining after welding or cold working may be relieved effectively by heat treatment. The temperatures of heat treatment and the holding times depend on the composition and thickness of the metal and the particular service for which it is intended. Cooling after heat treatment must be slow. There is slight variation in the different codes for stress-relief anneal. One such generalized procedure is given below:

Material	Temperature, °C	Time, hr
Aluminium alloys	230-260	1
Brass	200-300	½ to 1
Iron	500-600	½ to 1
Stainless steel	730-870	1 to 2
Magnesium alloys	130-300	¼ to 1
Nickel alloys	600-650	½ to 1

A number of cases have been reported where thermal stress-relief of industrial equipment has prevented stress-corrosion cracking. Thus, in a plant<sup>9</sup> manufacturing ammonium nitrate, drying and cooling drums made of carbon steel, which were heat-treated after welding, did not undergo stress-corrosion cracking, whereas failures occurred in welded parts which were not stress-relieved. The resistance to cracking of welded parts of carbon steel equipment in alkaline solutions has also been found to increase greatly when they are annealed.<sup>28,29</sup> The stress-corrosion cracking of an equipment made of type 316 stainless steel in a medium containing calcium sulphite, sulphur dioxide and traces of chloride was successfully prevented<sup>30</sup> by thermal stress-relief. In another case cracking of heating coils made of type 316 stainless steel in a phenol manufacturing plant was prevented by stabilising annealing at 870°C.<sup>31</sup>

Thermal stress-relief by muffle annealing cannot be applied where large or complicated equipment is in-

volved. Shot-peening has been found to be effective in many such cases. The process consists in propelling by a centrifugal impeller or by an air blast shot uniformly round (.007" to .066" dia.) at a controlled velocity against the surface of the metal. A compressive stress is thereby produced at the surface and cracking is minimised, since only tensile stress causes corrosion cracking. The examples may be cited: prevention of stress-corrosion cracking of type 410 stainless steel,<sup>32</sup> and low alloy martensitic steel<sup>33</sup> by shot-peening. Controlled low temperature stress-relieving of welded equipment, which cannot be furnace-annealed at higher temperature, has also been developed.<sup>34</sup> In this process two oxyacetylene torches are allowed to move in tandem along two strips one on each side of a welded joint so that they are heated to about 260°C.

In some cases, however, stress-relief does not seem to be of much use. Thus, Staehle, Beck and Fontana<sup>35</sup> have shown that austenitic stainless steel of type 347 will undergo transgranular stress-corrosion cracking at a stress as low as 2000 psi under vapour condensation conditions in presence of water at 204°C containing as low as 50 ppm of chloride. Uhlig and Lincoln<sup>36</sup> also report that austenitic stainless steel may fail by stress corrosion in chloride-containing water at elevated temperature under a stress as low as 500 psi.

(3) *Changing Corrosion Environment*: Since the equipment is intended for service under specified conditions, there is usually not much scope for avoiding stress-corrosion cracking by changing the corrosion environment. Sometimes this may be feasible e.g. by the use of demineralized water in place of water containing considerable amount of chloride, stress-corrosion cracking may be prevented in some cases. Another instance is the provision of keeping thermal insulation dry to prevent stress corrosion of austenitic stainless steel in contact with chloride that is liable to be leached out from insulation.<sup>26</sup>

Among other methods for preventing stress-corrosion cracking of metals, cathodic protection appears to be the most promising one<sup>15,29</sup>. This method can at least be applied to localized regions where the liability to cracking is high.

## Conclusions

The present position regarding stress-corrosion cracking of metals is that although conditions leading to this type of failure are fairly well known, satisfactory ways of solving the problem in practice are still often difficult to find. It is unfortunate that this type of corrosion puts a limitation on the use of engineering metals like austen-

tic stainless steel in certain environments. Much useful work is, however, being carried out in different parts of the world on elucidating the mechanism of stress-corrosion cracking. It is hoped that with a better understanding of the mechanism it will be possible to solve completely the problem of stress-corrosion failure of metals.

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# Calcium Ammonium Nitrate with Higher Nitrogen Content

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The handling of ammonium nitrate, a widely used fertilizer involves explosion hazards, and therefore it is generally blended with pulverized limestone, thus obviously increasing its cost. Yet there is a school which believes that dilution is not necessary while other precautions must be taken for its safe handling. The author after discussing the explosivity of ammonium nitrate has suggested a safe limit for its proportion—up to 22 per cent nitrogen—in an ammonium nitrate limestone mixture. Any increase in nitrogen content may not be a wise step at this stage when users are unaware of the inherent dangers involved.

Calcium ammonium nitrate, being produced at the FCI's Nangal and Rourkela plants, is a mixture of 60 per cent ammonium nitrate with 40 per cent of pulverised limestone (by weight) containing 20.5 per cent nitrogen. Addition of such a large amount of limestone, which is useless agronomically, increases considerably cost of production, packing, freight and distribution calculated on the basis of nitrogen content. The preference for calcium ammonium nitrate, over fertilizer grade ammonium nitrate is due mainly to the explosion hazards associated with the handling of pure ammonium nitrate. Over thirty explosions are on record involving fertilizer grade ammonium-nitrate.

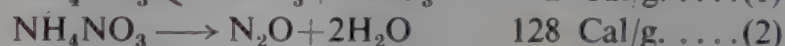
Desirability of diluting ammonium nitrate is not without controversy. Some believe that handling of ammonium nitrate can be rendered safe by taking necessary precautions, hence dilution is unnecessary. There are others who are in favour of dilution. The former view prevails in the U.S.A. and U.S.S.R where undiluted ammonium nitrate is being produced. The latter view has its adherents in U.K. and in many of the countries of the continent where the practice is to produce only the diluted product. At present an overwhelming proportion of the diluted material produced contains 20.5 per cent nitrogen.

Recently a suggestion has been put forward for increasing nitrogen content of calcium ammonium nitrate, produced at Nangal and Rourkela, from 20.5 to 26 per cent. The production of calcium ammonium nitrate of higher nitrogen content is an economically attractive proposition, and discussion of issues involved appears to be worthwhile.

## Explosivity of Ammonium Nitrate

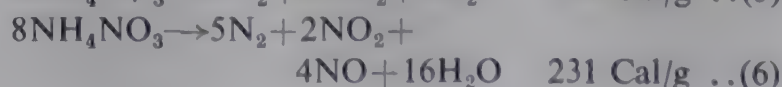
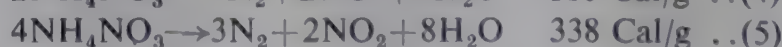
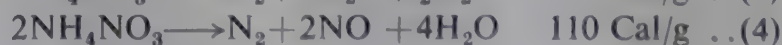
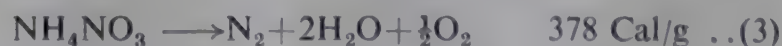
All the inorganic nitrates act as oxygen-carriers, and under favourable conditions these are capable of supplying their oxygen to other materials. Ammonium nitrate in addition is also capable of detonating under certain conditions. It is an explosive, although very insensitive to impact and difficult to detonate. It is, however, used extensively as an important constituent for industrial explosives.<sup>1</sup>

The normal decomposition of ammonium nitrate by thermal means leads chiefly to following reactions:



The reaction (1) is highly endothermic and (2) is weakly exothermic. As a result of these two concurrent reactions, the molten mass of ammonium nitrate tends to reach a steady temperature and there is little tendency towards self-accelerating decomposition or even continued reaction after the source of heat is removed.<sup>2,3</sup> Consequently, localised heating even to a high temperature is not likely to be dangerous. It has been shown that pure ammonium nitrate, without confinement, does not explode even when heated up to 410°C<sup>4</sup>.

Under conditions of confinement, highly exothermic reactions are known to occur<sup>5</sup> causing explosive decomposition of ammonium nitrate. The reactions are:



The essential conditions for the explosion of ammonium nitrate is stated to be that the temperature and confinement pressure should be around 300°C and 100 Kg/cm<sup>2</sup> respectively.<sup>6,4</sup> The role of confinement has not been fully understood, and various theories have been put forward. According to Hainer and Feik,<sup>3</sup> confinement represses endothermic dissociation of the salt, and the temperature rises till the explosive rate of decomposition is attained. The alternative view is that high pressure tends to retain the hot products near the zone of reaction and increase the rate of heat transfer to the undecomposed explosive and thus permit the development of hazardous temperature.<sup>7</sup> Both views may be correct as these are supplementary to each other rather than contradictory.

The temperature, which is required for the development of the rate of reaction to be of explosive violence, is of the order of 400°C to 460°C. The ease with which these temperatures are attained depend on the heat of reaction associated with the decomposition reactions. Any carbonaceous material like wax, paper, etc. if present, is oxidized violently by free nitric acid present, thus releasing considerable heat which brings down the limiting conditions of temperature and confinement pressure to 134°–153°C and 20Kg/cm<sup>2</sup> respectively.<sup>8</sup>

The conditions necessary for the explosion of pure ammonium nitrate may not be attainable during normal handling of the salt, but as shown above any contamination of the salt with sensitizing materials is liable to make the fertilizer dangerous.

After taking all these factors into consideration, decision was taken by the F.C.I. Ltd. to produce, to start with, only diluted ammonium nitrate.

#### Safe Limit

The most commonly used diluent is limestone. Limestone in calcium ammonium nitrate plays a dual role. Firstly, it brings down the nitrogen content to the acceptable level, secondly it desensitizes ammonium nitrate by preventing acidity to develop and thereby inhibiting further decomposition of the fertilizer.

Now the question arises as to the extent of dilution necessary in order to make the fertilizer completely safe. It has been shown by Braconier and Delsemme that the addition of limestone or chalk to the extent of 40 per cent by weight (20.5 per cent N) makes the fertilizer safe.<sup>9</sup>

The Underwriter-Laboratories of America have found that ammonium nitrate mixed with pulverised limestone in proportion 60 to 35 (22 per cent N) is entirely non-hazardous.<sup>9</sup> The work done at Linz (Austria) also

indicates that calcium ammonium nitrate containing 20.5 per cent nitrogen is completely inert, such is not the case with the product containing 26 per cent nitrogen.† The international agreement on railroad traffic freight of October 25, 1952 puts a limit of 65 per cent ammonium nitrate in the ammonium nitrate-inert mixture. Mixtures containing higher percentage of ammonium nitrate come under rigid regulations and are put in the category of inflammable materials. From the above, it may be reasonable to conclude that ammonium nitrate-limestone mixture containing up to 22 per cent nitrogen is completely safe.

#### Keeping Quality

Addition of 40 per cent limestone to ammonium nitrate does not make the diluted fertilizer less hygroscopic than ammonium nitrate,<sup>10</sup> but it increases its water-holding capacity. This decreases the caking tendency and improves the drillability of the fertilizer. In this respect, products containing lower percentage viz. 16 or 20.5 will fare better than those with 26 per cent nitrogen.

The disintegration of granules of ammonium nitrate on their repeated passage through the transition temperature of ammonium nitrate between forms IV $\longleftrightarrow$ III which occur at 32.3°C causes caking. This also occurs to a lesser extent in the diluted product. The disintegration on account of transition has been found to be more severe in the product containing 26 per cent than 20.5 per cent nitrogen. This aspect becomes more important to us in India, because of ambient conditions prevalent here with wide fluctuation in temperature, which often includes transition temperature.

#### Conclusion

Ammonium nitrate-limestone mixtures containing up to 22 per cent nitrogen is shown to be entirely non-hazardous, whereas the product containing 26 per cent nitrogen is not so. Increase in nitrogen content of calcium ammonium nitrate should be viewed dispassionately and with full realization of inherent danger associated with it, keeping in view the fact that users in this country are mostly illiterate.

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# Byproduct Ammonium Sulphate from Coke Oven Industries\*

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With the development of the synthetic ammonia industry, contribution of the byproduct ammonia towards the total nitrogen production has decreased gradually, but since coal carbonisation is essential for the steel and foundry industries and for town gas generation, production of by-product ammonia has continued. The processes for recovery of ammonia from coke oven plants and production of ammonium sulphate have undergone many improvements, and out of three such processes, viz. indirect, direct, and semi-direct, the last one has been adopted widely in view of its several advantages over the other two.

The byproduct ammonium sulphate was the only source of ammonia in India till 1938, when the first synthetic ammonia plant was installed at Belagula in Mysore. With the increase in the requirement of the nitrogenous fertilizers, more synthetic ammonia plants were set up viz. at Alwaye, Sindri, Nangal, Sahupuri, Rourkela, etc. and some more are now under installation. Till 1956, the installed capacity of byproduct ammonium sulphate plants was 29,070 tonnes per year constituting about 8 per cent of the total ammonia production in the country. By the end of 1966, the potential capacity of these plants will be of the order of 36,000 tons of nitrogen—equivalent to about 174,000 tons of ammonium sulphate—constituting about 5.5 per cent of the total nitrogen production and about 21 per cent of the total ammonium sulphate production based on the target production of 650,000 tons of nitrogen. The production of ammonia from steelworks' coke oven units, constituting about 40 tons of ammonium sulphate per ton of steel, will be quite a significant amount by the end of the Fourth plan.

Till the synthetic ammonia process of fixing atmospheric nitrogen was perfected, the entire supply of ammonia and its salts was obtained from the coal carbonisation industry as byproduct or recovered from the distillation of shale, peat, etc.<sup>1</sup> For instance, in 1910, the byproducts from coke oven plants furnished about 90 per cent of the ammonium sulphate produced in Germany, while the corresponding figures for the U.K. and U.S.A. were 60 and 20 per cent respectively.<sup>2</sup>

The first commercial synthetic ammonia plant was put into commission in 1913 in Germany<sup>3</sup> by the B.A.S.F.† World War I gave a great impetus to it, and since then there has been a phenomenal increase in the capacity of the synthetic ammonia industry.<sup>1</sup>

\*Paper presented at the ECAFE Conference on the Development of Fertilizer Industry in Asia and the Far East held in Bombay during November 18 to December 2, 1963.

†Badische Anilin & Soda Fabrik.

TABLE 1—WORLD PRODUCTION OF AMMONIA

Fertilizer Year	Output (metric tons Nitrogen)		
	Synthetic Ammonia	By-product Ammonia	Total World Nitrogen
1900	—	100,000	320,000
1910	—	210,000	570,000
1920	190,000	287,000	1,000,000
1925	345,300	324,900	1,152,000
1929/30	999,900	475,840	2,203,540
1930/31	852,822	390,534	1,694,288
1931/32	948,988	331,625	1,585,217
1932/33	1,140,325	297,279	1,676,859
1933/34	1,157,412	355,309	1,792,266
1934/35	1,264,184	360,334	2,041,366

SOURCE: I. Thorpe, J. F. & Whitley, M. A., Thorpe's "Dictionary of Applied Chemistry", Vol. I (1945), p. 33.

The contribution of coke oven byproduct industry to the total ammonium salt output has consequently declined very steadily (Table 1). The last decade has seen a further shift from ammonium sulphate to other ammonium salts or derivatives for fertilizer application (Table 2). Thus, by 1960 hardly 10 per cent of nitrogen output in U.S.A. came to be marketed as ammonium sulphate.<sup>5</sup>

In India, too, ammonium sulphate first featured as a byproduct of the steel plant coke ovens. At present there are some eight major installations,<sup>6</sup> which are either already producing ammonium sulphate as a byproduct or are installing ammonia recovery units (Table 3). The byproduct ammonium sulphate recovery plants in India have now an aggregate installed capacity of 85,770 tonnes/annum, while the actual output for 1961-62, which represented about 15 per cent of the total ammonium sulphate production, was 59,825 tonnes. With the setting up of synthetic ammonia units, however, the contribution of byproduct ammonium sulphate to the total nitrogenous fertilizer production in India will show the same trends as in the rest of the world.

#### Recovery of Ammonia from Coal Carbonisation Industry

The ammonia obtained in the carbonisation is mainly derived from the decomposition of nitrogenous organic

matter in coal. Normally, coal contains about 1 to 2 per cent of nitrogen, about 15 to 20 per cent of total nitrogen present in coal (or approximately 5.5 to 6.5 lbs. of  $\text{NH}_3$  per ton of coal coked) being recoverable in the byproduct coal carbonisation plants.<sup>7,8</sup> At least 50 per cent of the nitrogen present in coal remains in the residual coke and a good proportion of it escapes as gas, formed mainly by the decomposition of ammonia.<sup>9</sup> A small proportion of nitrogen distils over in the form of cyanogen, pyridine and other nitrogenous substances.

The formation of ammonia takes place mostly after the coking of coal is completed, say over  $900^\circ\text{C}$ ; so for its recovery, mainly the high temperature carbonization is to be considered. The distribution of nitrogen of the coal in the various products of carbonisation is as follows: In coke 50, in gas as free nitrogen 27.5, as ammonia 18.0, in tar 3.3 and as cyanides 1.2 per cent approximately.<sup>9</sup>

In the coke oven plants the hot gases from the ovens are cooled by spraying recirculated flush liquor. The condensed liquor and tar are separated from the gas, which is further cooled to condense out more liquor and tar. The cooled gas is either scrubbed by direct contact with water producing a weak ammonia liquor or it is passed directly through a saturator containing

TABLE 2—WORLD PRODUCTION OF NITROGENOUS FERTILIZERS (AS N), TONNES

Country	Output	1954-55	1955-56	1956-57	1957-58	1958-59	1959-60*
U.K.	Total	304,521	309,487	334,049	346,960	335,700	400,000
	Amm. Sulphate	218,173	215,833	230,378	237,119	227,400	220,300
U.S.A.	Total	1,811,875	2,029,607	2,059,000	2,141,000	2,448,000	2,605,000
	Amm. Sulphate	323,820	389,500	355,000	332,000	331,000	264,000
W. Germany	Total	745,300	752,200	895,400	1,047,400	1,050,700	1,051,000
	Amm. Sulphate	149,500	165,000	184,300	223,200	233,600	214,500
Japan	Total	632,535	704,429	780,460	882,807	986,260	932,280
	Amm. Sulphate	440,303	462,557	500,640	538,334	576,870	513,660
India	Total	83,115	81,688	80,820	80,838	80,835	
	Amm. Sulphate	83,115	81,688	80,820	80,838	80,835	
Total World Production		6,730,000	7,200,000	7,850,000	8,570,000	9,390,000	9,820,000

\*Preliminary figures

Source: *Fertilizers: An Annual Review of World Production, Consumption and Trade* (F.A.O.) 1960.

TABLE 3—INSTALLED CAPACITY OF BYPRODUCT AMMONIUM SULPHATE IN INDIA, TONNES

Sl. No.	Industries	Location	Installed Capacity of Ammonium Sulphate		Nutrient (N)		Additional Available Potential Capacity	
			1956	1962	1956	1962	Material	Nutrient N
1.	Tata Iron & Steel Co. Ltd.	Jamshedpur, Bihar	15,490	21,900	3,190	4,510		
2.	Indian Iron & Steel Co. Ltd.	Burnpur, W. Bengal	9,390	21,120	1,930	4,350		
3.	Indian Iron & Steel Co. Ltd.	Kulti, W. Bengal	1,680	—	350	—		
4.	Barrakur Coal Co. Ltd.,	Bansjora, Bihar	1,340	1,340	280	280		
5.	Bararee Coke Co. Ltd.,	Bararee, Bihar	1,170	1,170	240	240		
6.	National Coal Development Corpn., (formerly E. I. Railway)	Giridih, Bihar	—	—	—	—		
7.	Hindustan Steel Ltd.,	Bhilai, M.P.	—	20,120	—	4,140		
8.	Hindustan Steel Ltd.,	Durgapur, W. Bengal	—	20,120(1960)	—	4,140		
9.	Fertilizer Corporation of India Ltd.	Sindri, Bihar	—	—	—	—	3,300	680
10.	Hindustan Steel Ltd.,	Rourkela,** Orissa	—	—	—	—	20,120	4,140
11.	Durgapur Industries Ltd. (W. Bengal Govt.)	Durgapur, W. Bengal	—	—	—	—	5,000	1,030
Total			29,070	85,770	5,990	17,660	28,420	5,850

Source: 1. *Fertilizer Statistics*. Fertilizer Association of India, New Delhi (1956, 1960, 1961-62)

2. *Year Book of Coke Oven Managers' Association, U.K., 1954.*

sulphuric acid for the production of ammonium sulphate. The following are the three processes<sup>9</sup> for ammonia recovery from coke oven plants: (a) Indirect process; (b) Direct process and (c) Semi-direct process.

(a) *Indirect Process*: In the early days of byproduct ammonium sulphate production from coke ovens, the hot gases from the coke ovens used to be cooled by the recirculating flush liquor, whereby the liquor and major portion of tar was condensed out. Thereafter, the gases were further cooled to remove the residual tar and liquor and then scrubbed with water to remove ammonia in the form of weak ammonia liquor. During scrubbing some portions of hydrogen sulphide, cyanides, pyridine, etc. were also absorbed in the liquor. The combined liquors were stripped in ammonia still with a lime leg to recover the free and fixed ammonia, while vapours from the still were either condensed to form crude concentrated ammoniacal liquor or directly passed through a saturator containing sulphuric acid to convert the ammonia to ammonium sulphate. The saturators were operated normally at about 100°C. The ammonium sulphate slurry was taken out, centrifuged, washed and dried. In later developments, in some plants pyridine was also recovered from the mother liquor.

(b) *Direct Process*: In view of the complicated set-up, high capital investment and the problem of disposal of large quantity of waste liquor, alternative processes were developed for absorbing ammonia directly in sulphuric

acid. In this process, the hot gases from the coke ovens were allowed to condense out the major portion of their tar content without using a flushing liquor. The hot gases containing all the ammonia and appreciable quantity of tar were allowed to pass through a saturator containing sulphuric acid for the recovery of ammonia in the form of ammonium sulphate and then the outgoing gases were condensed to remove liquor and residual tar. Several modifications were made to overcome difficulties encountered in this process. The process, however, continued to pose problems such as condensing of tar in saturator, corrosion of the saturator and accessories due to the formation of hydrogen chloride by the decomposition of ammonium chloride, inferior quality of the byproduct ammonium sulphate and the tar. Of course, in this process ammonia liquor as such was produced in quantities small enough not to create any major liquor disposal problems.

(c) *Semi-direct Process*: Subsequently, the direct process was almost abandoned giving place to semi-direct process. In this process, the hot gases evolved from the ovens were cooled by a spray of circulating flush liquor, whereby most of the fixed ammonium salts were removed and major quantity of tar was condensed. The gases were further cooled for the removal of more tar and liquor. The condensed liquor, containing both free and fixed ammonia, was distilled in reaction with lime when both free and fixed ammonia were stripped out as vapour. The hot vapour was mixed

with the remaining coke oven gas, preheated to a temperature of 70 to 75°C and passed through a saturator containing sulphuric acid maintained normally at 45 to 70°C. Ammonium sulphate, thus formed, was removed in the form of a slurry, centrifuged, washed and dried. The gases leaving the saturator were practically free from ammonia and were processed for benzole recovery and for further purification. In this process the ammonium sulphate is of better quality. In some plants the pyridine was also recovered from mother liquor. The relative merits and demerits of the three processes are given in Table 4.

steam-heating of the saturator has to be resorted to prevent dilution of the bath. The saving of steam is often counterbalanced by increased power consumption. The process has no flexibility, and for that matter need not be recommended. It has never been used in the U.S.A. and has also been virtually abandoned in Europe long ago.

The indirect process has maximum flexibility, specially for the production of crude concentrated ammonia liquor or many other ammonium salts. Moreover, its operation is not tied up with or dependent on other operations of the carbonisation process and, finally tar

TABLE 4—RELATIVE MERITS AND DEMERITS OF THE DIRECT, SEMI-DIRECT AND INDIRECT PROCESSES OF AMMONIA RECOVERY

	<i>Direct</i>	<i>Semi-direct</i>	<i>Indirect</i>
1. Capital Investment	Lowest	Lower than the indirect process	Highest
2. Operating Costs	Lowest	Lower than the indirect process	Highest
3. Ground space requirement	Least	Less than the indirect process	Largest
4. Degree of ammonia recovery	Maximum. Equal to the semi-direct and 5% higher than the indirect process.	Almost equal to the direct process and 5% higher than the indirect process	Minimum due to loss of ammonia at the scrubbers, from storage and at the stills.
5. Corrosion problems	Maximum. Specially due to hydrogen chloride from decomposition of ammonium chloride.	Less than the direct process	Minimum
6. Purity of products			
(a) Ammonium sulphate	Badly contaminated and of inferior quality.	Better quality with lesser contaminations	Superior quality free from most of the contaminations
(b) Tar	Badly affected	Not affected	Not affected
7. Utilities consumption			
(a) Steam	Lowest	Lower than the indirect process	Highest
(b) Power	Maximum		
8. Disposal problems of effluent liquor	Minimum	Greater than the indirect process Appreciably less than the indirect process	Minimum Maximum
9. Operational flexibility and problems	Nil and insurmountable practical difficulties	Some elasticity. More reliable than the direct process and almost as reliable as the indirect process	Maximum elasticity and most reliable.

## Discussions

Among the three processes described above, the direct process has the smallest capital investment and operational costs, least ground space requirement and lowest steam consumption. In this case, ammonia recovery is equal to that in the semi-direct process and about 5 per cent higher than in the indirect process. Among the disadvantages, the major one is the severe type of corrosion of equipment due to the formation of hydrogen chloride. The quality of tar is affected adversely on account of the concentrated sulphuric acid in the saturator, and the ammonium sulphate gets contaminated with tar and is coloured due to organic and inorganic impurities. The operation is also beset with problems, many of which are often unforeseen. Frequent

removal is complete. On the debit side, are the production of a large volume of waste liquor, which is more than double than in the case of the semi-direct and as much as 16 times than in the direct process, high steam consumption and operating costs, large capital investment and space requirements and loss of ammonia from scrubbers, storage and at the still.

The semi-direct process has several advantages over other two processes. It has flexibility since products other than ammonium sulphate can also be made, though to a limited extent. The capital and operating costs are lower, less ground space is required, steam consumption is lower and ammonia recovery from the gases is higher by 5 per cent (even 12 per cent has been reported) over the indirect process. Cheaper 60° Be

acid can be used in the saturator and the dilute acid has no effect on gas components. At present practically almost all the recovery plants are operating on either semi-direct or indirect process.

Many modifications of the ammonia recovery processes have been carried out to overcome the disadvantages of the existing ones, mainly to reduce the volume of the weak ammonia liquor, thereby reducing the still waste liquor disposal problem and the consumption of steam. These have been attained by: (a) the provision of heat exchangers utilizing the sensible heat of the still waste liquor, (b) ammonia removal by cooling the gas to  $-10^{\circ}\text{C}$  to  $10^{\circ}\text{C}$  whereby a concentrated liquor of 6 per cent ammonia was produced. Here, in addition to reduction of liquor volume, tar, naphthalene and moisture are removed completely from the gas, (c) in recent years a process for the recovery of ammonia from weak ammonia liquor by the cation-exchange technique has been developed and is being used on a commercial scale.

In the early days, ammonium sulphate produced from the byproduct industry was of inferior quality, and gave rise to caking of the product. This was variously attributed to the presence of moisture, free acid, pyridine sulphate and to improper crystal size, etc. While moisture was eliminated by means of driers, drying alone caused an increase in sulphuric acid concentration, which again picked up moisture during storage. It was also observed that pure ammonium sulphate is not hygroscopic, but it becomes increasingly so with increasing free acid content. Pyridine sulphate, invariably present in the ammonium sulphate, is a source of free acid which causes caking. This acid was neutralized with free ammonia during drying which also removed the pyridine. A dirty coloration of the product badly affected sales appeal of the product. The brown colour developed was due to materials of organic origin and blue colouration due to complex iron cyanides. A point to be noted is that the presence of free acid necessary in the saturator for prevention of blue salt formation as well as for better ammonia absorption ultimately posed problems of caking of the salt.

### Scope of Byproduct Ammonium Sulphate Industry in India

Prior to the installation of public sector steel plants, byproduct ammonium sulphate was produced by the coke ovens of T.I.S.Co. at Jamshedpur (1907), I.I.S.Co. at Burnpur (1918) and at Kulti, Bararee Coke Co. (1921), Barrakur Coal Co., and N.C.D.C. at Giridih.<sup>10</sup> Before 1950 these plants were producing about 25,000 tons of byproduct ammonium sulphate per annum.

In 1956 these plants had a total installed capacity of 29,070 tonnes for byproduct ammonium sulphate per annum which constituted only 8 per cent of the total ammonia production in the form of ammonium sulphate at that time. With the installation of public sector steel plants and expansion of the existing private sector steel plants, the potential capacity of the byproduct ammonium sulphate has increased from 29,070 (1956) to 85,770 tonnes in 1962 per annum. In 1961-62 the actual production of total nutrient nitrogen was 149,019 tonnes compared with 82,472 tonnes of nitrogen nutrient as ammonium sulphate of which 12,320 tonnes was produced in the form of byproduct ammonium sulphate (Table 5). Thus byproduct ammonium sulphate constituted about 15 per cent of total ammonium sulphate production and only about 8.5 per cent of the total nitrogen production.

TABLE 5—PRODUCTION OF NITROGENOUS FERTILIZERS IN INDIA FROM 1952-53 TO 1961-62, METRIC TONS

Year	Material Ammonium Sulphate	Nutrient (N)	(1)
		Ammonium Sulphate	Total
1952-53	257,609	52,810	52,810
1953-54	256,819	52,648	52,648
1954-55	332,417	68,145	68,145
1955-56	373,108	76,486	76,486
1956-57	387,466	78,406	78,406
1957-58	393,905	80,751	80,751
1958-59	392,069	80,374	80,374
1959-60	367,016	75,238	82,465
1960-61	399,270	81,850	107,955
1961-62	402,303	82,472	149,019

(1) Excludes production of ammonium chloride for which data are not available.

SOURCE: *Fertilizer Statistics*, 1961-62, Fertilizer Association of India, New Delhi (1962).

The latest figures indicate a possible achievement of 650,000 tons of total nitrogen nutrient by 1966,<sup>11</sup> compared to 173,430 tonnes of nitrogen nutrient production in the form of ammonium sulphate. During this period, due to the expansion of the existing steel plants, by-product ammonium sulphate from the coke ovens will be increased to 36,000 tons of nitrogen. It could be seen, therefore, that by 1966 byproduct ammonium sulphate will constitute about 21 per cent of the total ammonium sulphate and about 5.5 per cent of the total nitrogen production. Thus, it seems that even with the increase in the production of the synthetic ammonia fertilizers, byproduct ammonium sulphate potentialities cannot be ignored.

It has been observed in the above paragraph that, with the development in the nitrogenous fertilizer industry, the production of synthetic ammonium sulphate has been gradually reduced in comparison to total synthetic nitrogenous fertilizers. This has been due mainly to the scarcity of indigenous sulphur for production of sulphuric acid in the country, non-availability of good quality of gypsum reserves and changes in pattern of consumption of nitrogenous fertilizers. But with the rapid industrialisation, demand for steel has increased at a rapid rate, necessitating the installation of new steel works and increasing the capacities of the existing ones. An essential requirement of steelworks is the metallurgical coke which can only be obtained by the high temperature carbonisation of coal. Thus with increase in steel production, there will be a proportional increase in the coal carbonisation potential, thereby increasing the production of by-product ammonium sulphate. Nearly 40 lbs of by-product ammonium sulphate is obtained per ton of steel production. Thus, for every 1 million ton of steel production, approximately 20,000 tons of byproduct ammonium sulphate will be obtained. Ten to twenty million tons of steel production in future will increase the byproduct ammonium sulphate production from 2 to 4 lakh tons per annum which is certainly not a negligible amount compared with the total nitrogen production in the country. Moreover, recovery of ammonia is also associated with problems of effluent disposal. With this end in view in the recent years investigations are being carried out all over the world to improve the efficiency of the production of byproduct ammonium sulphate and reduce its cost of production by recovery of other ingredients present in the coke oven gas. Out of these, recovery of pyridine has been found to be most encouraging.

Work has already been carried out on pilot plant scale in some western countries on the recovery of ammonia from coke oven liquor by the use of cation exchangers. Augsburg Gasworks in Germany<sup>12</sup> have already set up a commercial plant on this process for the recovery of byproduct ammonia with a capacity of 5 tons per day by treating 145 cu. metres of ammonia

liquor. This process claims simplicity of operation, lesser production cost and relative ease of the disposal of the effluents.

Recent data obtained in this laboratory show that recovery of this ammonia by cation exchanger could be profitably made with the use of a cheaper cation exchange material prepared from the coke oven waste product, thereby reducing the cost of production to an appreciable extent. Thus, it could be seen that byproduct ammonium sulphate industry in India under no circumstances could be completely ignored vis-a-vis the synthetic ammonia industry either from the consideration of the quantity produced or from cost. In fact, in the present food shortage steps for obtaining every ounce of fertilizer from every source have to be tapped for meeting the total fertilizer requirement.

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# Civil Construction of Fertilizer Factories

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This article gives a brief account of the problems of organisation and construction of fertilizer plants to achieve a quick execution so as to commission them according to schedule.

## General

Modern chemical works involve a complex set-up both in their design and execution. The construction of industrial buildings and plants differs from all other civil engineering structures as this requires collaboration of specialist-designers from different branches. The preparation of drawings and specifications, to be embodied in an industrial plant, are the result of co-operation between the architect and the structural engineer together with a large group of specialists concerned with the layout of the technological equipment, instruments, electric and other supplies, conveyors, production units, heating, ventilation, etc. The construction engineer in-charge of the project will have to coordinate the activities of a host of disciplines in order to meet the requirements of the various branches and to achieve the desired objective of the project.

The F.C.I. Ltd. have erected two new factories—one at Nangal and the other at Rourkela—apart from the Sindri works which was built some time back. Four other factories, viz. at Trombay, Namrup, Gorakhpur, and Korba, are in various stages of execution. The organisation necessary for the construction of these giant fertilizer units has to grapple with the manifold problems and complexities inherent in such a chemical industry. The quick constructional activity would be possible only if the standardisation of the plants could be achieved. But with the varied elements like the raw materials, chemical processes and the designed end-products, standardisation is perhaps a difficult affair. Lack of standardisation has an impact on the difficulties of construction of such heavy chemical plants.

## Planning

During the planning of such giant units all the problems of construction cannot be foreseen till the process raw materials and end-products are clearly

defined. It normally takes over 4 years from the time a project is conceived till it is finally brought into stream. Within these years, varied disciplines will have to work simultaneously in an integrated manner to achieve the target of designing and the establishment of the factory. The actual construction, after the planning is finalised, will normally have to be completed within a period of 2 to 3 years. On an analysis of the projects like those at Nangal (already on stream), Trombay and Gorakhpur, it is revealed that approximately 30 to 35 per cent of the project costs are involved in constructional activities, apart from the costs of the main plants, their ancillary equipment like workshop machinery, tools and miscellaneous expenditure viz. on services and establishment, etc.

Out of the 30 to 35 per cent of the construction costs, approximately 25 per cent are involved in civil works like the development of land, railway siding, water-supply system both for the factory and the township, structural work in the factory including special types of foundations and non-plant buildings which shall also include building of the township providing residential houses, shopping centres, schools, hospitals, suitable roads and bridges, drainage, levelling, underground sewers, water distribution and sewage disposal. The balance of the 10 per cent of the construction cost is approximately divided in the ratio of 6 to 7 per cent towards mechanical erection and 3 to 4 per cent for electrical erection.

Although constructional activity forms only 30 to 35 per cent of the cost, it is vital for the completion of a project. Civil works, comparably a small affair compared to the total cost of the project, form a vital base for the erection of the factory. The organisation for the civil works is an important factor in the construction activities, so as to obtain the erection work within the scheduled period.

## Site Selection

An essential factor in the establishment of a fertilizer factory is the selection of its site, which is based, apart from other considerations, mainly on the following factors: (1) Proximity of raw materials; (2) availability of land; (3) water supply facilities; and (4) availability of power. Of these, the proximity of raw materials and the availability of land are more important. These are met rarely within the limits of an existing town.

A large factory would invariably involve employment of a large personnel, say 2500 and above. Living accommodation for such a large personnel will have to be arranged both in the interest of the welfare of the workers and the efficient running of the factory. For providing living accommodation to such a complement of personnel, an associated township becomes a necessity. On an analysis from the data available on the projects executed so far, it is found that the cost on a township will rarely exceed 10 per cent of the cost of the whole project.

## Town Planning

This brings in the immediate necessity of an intelligent and imaginative master plan which integrates the factory and the township. The town-planning calls for a correct understanding of modern industrial problems, successful solution of which brings in happy and cooperative relationship between the factory management and the staff. The town-planners and architects will have to plan the township within the economic limits of investment. The density of population of the township should be kept within an acceptable limit but should not decrease to such a level ultimately resulting in increased development cost. Provision for all modern amenities like protected water-supply, underground drainage, surface drains, schools and colleges, shopping centres within easy reach of the various sectors of the township, hospital with dispensaries in different sectors, recreation centres like clubs, playgrounds, parks, etc. will have to be made in the township. In addition, the planner has also to keep in view any proposals for future expansion of the works.

## Civil Engineering Work

The civil engineering wing of the construction organisation will have to handle almost the entire range of civil engineering activities viz. railway siding, head-works and purification works in the factory and the township, water-supply distribution both in the township and the factory, the entire design and execution of underground drainage and disposal of rain water,

sewage and effluent, foundation and structural work in the factory.

The civil engineering activities may occasionally call for a change from the normal engineering construction organisation, keeping in view that the project has to be executed in the shortest time.

The design of civil works and the factory cannot normally start till the plant suppliers furnish scope drawings for the various plant buildings. These drawings are expected to indicate positioning of the various machines and equipment as well as their weights. The positioning, including clearances, will have to be decided by the plant suppliers on the basis of their knowledge of the process involved as well as the operational necessities. The weight of equipment will not be available with the suppliers of plants till their contract has been finally accepted. In most cases, the plant suppliers would not be the manufacturers of the equipment but would be ordering the various units from specialised machinery and equipment manufacturers. This means, they will have to rely upon the vendors' details before they can pass on the equipment and machinery details necessary for finalising the foundations as well as the plant buildings. This is an inevitable and time-consuming process, during which the construction work cannot be started.

In certain cases, where the soil condition does not permit open foundations but involves the use of piles, the important machine foundations like those of heavy compressors will have to be finalised before any important plant constructional activity can be started. These limitations, which are peculiar for such heavy chemical plants, will have to be taken care of in the execution of the factory foundations and structures.

In normal civil engineering activity, the design drawings and detailed estimates with specifications are finalised before the contract is given for erection of the plants. This procedure is hardly possible in view of the difficulties explained earlier in finalising the plant foundations and structures. It normally takes 3 to 4 months before the detailed designs, drawings and estimates are prepared after getting the necessary information about the positioning and weights of the various machinery and equipment in the plant buildings and then calling for tenders and fixing up of the contractor. To overcome the inevitable time-loss between the availability of details and starting of the construction, either of the following alternatives may be followed: (1) to construct the entire factory structures and foundations departmentally; or (2) to fix up a contractor on the basis of scope drawings and scope estimates well in

time specifying his responsibility for starting the execution as and when the detailed design drawings are made available.

The departmental execution of the factory foundations and structures would present many organisational problems, of which the purchase of materials and machinery required for the construction, and a large technical personnel that would be required to take over the function of both the inspection and the contractor, are the major ones. Unless purchase procedures are simplified or the chief of the construction activities is empowered to make purchases without going through the normal purchase procedures, it will present insuperable difficulties in maintaining the time-schedule and the cost of construction. Any delay in the purchase of the required materials at the specified times would inevitably involve loss of time and also waste of labour. A more difficult problem would be the recruitment of technical personnel of desired qualifications and experience. The demand of technical personnel in departmental execution will be very much more than for the management and supervision of contracts. The construction activities tail off at the end of the project, and it becomes a problem how to engage the technical personnel to the fullest advantage, unless there are other projects which have been planned in such a way that the services of technical personnel could be transferred to them in a phased manner.

The only other method of execution is to give the construction jobs to different contractors, maintaining only a skeleton of technical staff for the supervision of their work. For achieving quick execution, a single contractor may be engaged. Both at Nangal and Trombay, it was possible to select a civil works contractor out of the tenderers of the plant suppliers. For that matter the tender document should incorporate a complete specification of all anticipated items of construction, based upon previous experience in a factory of similar magnitude, with quantities which might vary depending upon final designs, drawings and estimates. A contractor would then be in a position to quote for the possible items of construction, fully aware that the quantities would vary and that he would have to execute even if the final drawings differ considerably from the scope drawings. There may arise many non-

tendered items of construction jobs for execution, so the contract should provide a method of quick and fair settlement of such items also.

Both the owner and contractor would, no doubt, be undertaking a certain amount of risk in such type of contracts, as the items of jobs for execution would differ from the tendered ones. The main advantage of such a procedure would be that the contractor would be able to start the construction work as soon as the detailed drawings are made available. This will also enable coordination between the civil works and the mechanical and electrical erection jobs which can start simultaneously without creating a friction between the two agencies. Such a method of execution calls for tact and understanding on the part of the construction engineer.

### Coordination

The most difficult part of the organisation and management of constructions where several disciplines are involved is coordination. Friction between the various agencies involved is inevitable in such an arrangement, but to eliminate it various methods of coordination have to be evolved. For example, at Nangal, a tally-card system was introduced wherein the civil works contractor, civil works supervisors and the mechanical erection wing would check up and certify the position of the various inserts before the concrete was poured. A check for the positioning would thereby be certified by all the parties concerned. This worked satisfactorily as the mechanical erection wing was associated closely with the civil construction wing and the defects used to be rectified by all the parties before signing the tally card.

The other more important method of coordinating the progress of work would be the holding of weekly or periodical meetings. Incidentally, such important problems, e.g. purchase of raw materials and equipment could also be solved in such meetings.

The construction wing will have to carry through all those concerned in the hectic activities that will have to be maintained from the start to the final stages of erection till the factory goes into production.

# Agronomical Significance of Carbon Nutrition\*

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Evidences suggest that carbon is taken up through the roots and actively metabolised inside the plant system which is beneficial for plant growth and results in high carbohydrate yield. In practice, possibilities exist to increase crop yields by supplying carbon artificially either through the application of organic carbonaceous sources or through carbonate and bicarbonate salts.

The investigations of Theodore de Saussure<sup>1</sup> brought into light the importance of carbon nutrition in the plant kingdom. He grew plants in air and in known mixtures of carbon dioxide, and measured the changes in the composition of the gases by eudiometric analysis and the changes in the composition within the plant by "carbonation". He concluded that carbon dioxide in small quantities was a vital necessity for plants and that they perished when they were devoid of it.

Humphry Davy<sup>2</sup> believed that plants, of course, derived some of their carbon from air, but the major portion is taken up through the roots. He was the first to recognise that carbon nutrition may also take place through the roots.

Since then, scientists have concentrated their investigations on this branch of science and also on the photosynthetic fixation of carbon dioxide which is of vital importance for green plants. Soon it became accepted that the free air is the only source of carbon dioxide for the plants. However, a minority of the scientists began to disagree with this view, and indicated that a portion of carbon dioxide reduced in green leaves had been derived from the soil. Boussingault<sup>3</sup> in 1844 suggested that the atmospheric carbon dioxide is the only source of carbon for the photosynthesizing plants, while in 1855 Unger<sup>4</sup> pointed out that this carbon dioxide would not account for all the carbon assimilated by plants.

The first attempt to demonstrate carbon nutrition through the roots was made by Birner and Lucanus<sup>5</sup> in 1866 by introducing carbon dioxide into the nutrient solutions in which *Avana sativa* plants were growing. This caused a better rate of growth and development and produced higher dry-matter yields compared with similar cultures receiving no carbon dioxide. They came

to the conclusion that the extra carbon dioxide was absorbed through the roots and exerted a favourable influence on the production of organic material in the plants. Free<sup>6</sup>, however, disagreed with this view. It was demonstrated much later that the injury to the plant on account of carbon dioxide introduction into the nutrient solution was probably due to the narrowing of the oxygen/carbon dioxide ratio in the solution.

In 1876, Bhom<sup>7</sup>, growing scarlet runner bean plants, some in sand and some in humus soil, concluded that carbon dioxide from the humus soil was not absorbed by the plant roots. However, he searched only for starch in the plant material. A year later Moll<sup>8,9</sup> confirmed his observations. Vines<sup>10</sup> in 1875 opined that no carbon dioxide translocation can take place within the plant body. He therefore concluded<sup>11</sup> that there is no experimental evidence which would tend to show that this absorption is under any circumstances possessed by plants or their parts, which are devoid of chlorophyll. More recently Poel<sup>12</sup> and others have demonstrated that plant roots can fix carbon from the nutrient solution when supplied with it.

Pfeffer<sup>13</sup> realised that during the process of transpiration, translocation of carbon dioxide may take place from the roots to the other organs of the plant. Ewart<sup>14</sup> confirmed it, and thought that carbon dioxide absorbed by the roots can easily be transported to the leaves and utilized in the process of starch synthesis. A major part of the carbon dioxide assimilated by plants is derived from the air and only a minute quantity absorbed by the roots may reach the leaves. However, he stressed the importance of root absorption of CO<sub>2</sub> by saying that "the amount derived from the roots may, when transpiration is active, be sufficient to prevent the chloroplastids in the more deeply situated tissues, at the base

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of a green stem, from losing the power of assimilating carbon dioxide when exposed to light for prolonged periods in an atmosphere free from this gas". Zijlstra<sup>15</sup>, using several plant species, demonstrated in 1909 that translocation of carbon dioxide from one part of the plant system to another can take place.

In 1909, Moll<sup>16</sup> contended that the minute quantity of carbon dioxide absorption through the roots cannot contribute appreciably to the synthesis of organic matter in the leaves. Mistscherlich<sup>17</sup> from his experiments with oats, grown in a soil culture, concluded that carbon dioxide has no direct influence on growth. He suggested that possibly it can exert an indirect influence by bringing more nutrients into solution which was also pointed out by many others.<sup>18</sup>

In 1917, Pollacci<sup>19</sup> reported a number of experiments in which he supplied the gas in the nutrient solution and kept the tops of the plants in an atmosphere devoid of it. He found that the plants receiving extra carbon dioxide had greater dry weights as compared with the seeds before they germinated. From these experiments he concluded that carbon dioxide absorbed by the roots of green plants may be the source of some carbon for starch formation. In 1929, Spoehr<sup>20</sup> observed that conditions may exist in which carbon dioxide absorbed by the roots may contribute to the total amount of the gas reduced by the plants.

Stoklasa<sup>21</sup> in 1927 recognised that carbon dioxide can be transported to the photosynthesizing organs through the stem, and stressed the quantitative importance of the gas absorbed by the roots which might sometimes be greater than that by direct absorption. He held that soil bacteria plays an important role in producing carbon dioxide in the soil which diffuses ultimately reaching the leaves as well as providing carbonate ions to the soil solution.

Bergamaschi<sup>22</sup> in 1929 confirmed Pollacci's observation using maple, linden, camellia and oleander and concluded that at least some of the carbon dioxide is absorbed through the roots. Later, she observed that when maize seedlings were supplied with carbon dioxide through the roots as well as the leaves, they yielded the highest carbon percentage in the dry weight (75.72) exceeding the value of carbon as that of dry weight (43.65%) in those plants which were treated with carbon dioxide through the roots, the tops being kept in an atmosphere devoid of it. The latter in turn exceeds the value in plants to which no carbon dioxide was supplied either ways (C. 39.3 per cent). The control plants kept in darkness had the lowest carbon content (34.86 per cent). Miller<sup>23</sup> also supports that a green plant may

absorb carbon dioxide from the soil and thus supplement its supply from the air. Raber<sup>24</sup> too has pointed the out possibility of carbon nutrition through the roots.

Livingston and Bell<sup>25</sup> after a thorough review came to the conclusion that with higher concentration of carbon dioxide in the soil solution with rapid transpiration, and with internal as well as external conditions otherwise favourable, a plant may receive from the soil as much as 5 per cent or even more of the gas through photosynthesis. They considered that the transpiration stream is the most probable means for the transport of carbon dioxide from roots to the leaves, and concluded that the plants treated with the gas were generally more vigorous than the untreated ones. They used soil cultures and maintained high concentration of the gas in the soil mass of some pots. The growth acceleration concomitant with this treatment was found very pronounced for plants of *Lupinus albus*, less pronounced in *Coleus blumi* and for *Lycopersicum esculentum*, slight for *Dracaena caderiana* and nil for a dark red form of *Coleus blumei*.

Wilson et al<sup>26</sup> have found that the addition of carbon dioxide to clover and lucerne resulted in an increase in the quantity of nitrogen fixed and that even a very small increase in the partial pressure of the gas ( $p\text{CO}_2$ ) produced large increases in the dry matter yield and the number of nodules formed. About 40 per cent of the carbon furnished was recovered in the plants. In a later experiment, Georgi et al<sup>27</sup> have confirmed that the effect of carbon dioxide on increased nitrogen fixation was due to an increase in  $p\text{CO}_2$  rather than to the total quantity of the gas. In both sand and agar cultures, the dry matter yield was almost double that of the controls receiving only  $\text{CO}_2$  free air. They<sup>27</sup> believed that the beneficial effect of the gas was in the formation of higher carbohydrate content and through another investigation they observed that the plants supplied with carbohydrates (glucose, sucrose and manitol) were stouter than those grown in the plain agar. This erectness was probably due to the reduction in the cell size after the treatment. They noted that during the time of harvest, the plants receiving the higher concentration of carbohydrates were red stemmed and gave evidence of carbohydrate excess, which was confirmed by Laurent<sup>28</sup> and Maze's<sup>29</sup> experiments indicating increased yields of vetch, maize and leguminous plants when supplied with carbohydrates. Finally, they concluded that in both agar and sand cultures, the addition of sucrose or glucose results in an increase in the nitrogen fixed by red clover plants. Plants grown in closed containers receiving 0.25 per

cent carbohydrates showed a definite increase in nitrogen fixation. With plants in open containers the increase was noted only in concentrations of about 0.5 per cent. This was probably due to less carbohydrate starvation in these plants, so that the added carbohydrates were less effective. They believed that the increase in yield and the nitrogen fixed was due to the following factors: (1) liberation of carbon dioxide due to bacterial activity and hence an increase in  $p\text{CO}_2$  available to the plants; (2) direct absorption of the carbohydrates resulting in an increase in the carbohydrate level in the plant sap, which is in complete agreement with Knudron's<sup>30</sup> findings.

An intensive investigation on aerial fertilization of carbon dioxide was undertaken during 1938 to 1940 and Molliard<sup>31</sup> using radish plants found that concentrations of carbon dioxide 5, 25, 100 and 500 times its normal content in air increased the yields of plants with the increased concentrations of the gas used. Richter and Elpidena<sup>32</sup> tried aerial fertilization of carbon dioxide on a field scale, and concluded that the plot so fertilized resulted in an increased dry matter yield.

Ravich et al.,<sup>33</sup> using products of catalytic combustion as fertilizers, have found that gaseous products of flameless combustion produced intensive growth of the plant. In the same year, Tiulin<sup>34</sup> concluded that the carbon dioxide of the soil air can be increased two to three-fold by the use of manures on the surface of the soil, and for the first time suggested that by the use of manures it is possible to fertilize plants with carbon dioxide.

In 1939, Katunsky<sup>35</sup> found that smoke gases with about 15 per cent of carbon dioxide are quite suitable for aerial fertilization of crop plants, and concluded that this fertilization was most effective when applied at those stages of development when the rate of accumulation of organic substances in the plant is greatest.

Yurbitsky<sup>36</sup> agreed with Tiulin and concluded that the favourable influence of manure on the cultivation of cucumbers was partly due to increased uptake of carbon dioxide by roots as well as by the aerial organs. Increased application of manure to sugar beet and the resultant increase in soil carbon dioxide led to an increase in the percentage and its yield of sugar, but decreased the yield and area of the leaves.

Ravich and Sarycheva<sup>37</sup> used combustion gases as fertilizers in a green house experiment with essential oil plants and found that carbon dioxide stimulated plant growth and branching and hastened flowering. It appears that this gas has an opposite effect to nitrogen because it enhances reproductive growth, whereas an excess of the latter delays it.

The investigations on the uptake of carbon dioxide using radioactive carbon undertaken by Overstreet et al.<sup>38</sup> have indicated that plant roots can fix carbon in the dark.

Ruben and Camen<sup>39</sup> found that many heterotrophic systems and non-green tissues of both plants and animals can retain free carbon dioxide and carbonic acid from solutions rich in these. Using short-lived radioactive  $^{11}\text{C}$  they demonstrated fixation of carbon dioxide by a preparation of barley roots. They failed to explain and evaluate the significance of this assimilation of carbon dioxide because of the short half life of  $^{11}\text{C}$ . Overstreet et al.<sup>38</sup> thought that the assimilation of carbon dioxide by barley roots in water suspension would have a direct bearing on the study of electrolyte accumulation by root cells. It admits the possibility of a considerable absorption of  $\text{HCO}_3$  ion by the non-photosynthetic root cells through a "process which results in the reduction and storing up of the carbon in the form of new organic compounds". They came to the conclusion that radioactive carbon, present in the culture solution, mainly as bicarbonate ion, was eventually assimilated by the roots of barley plants. Under their experimental conditions, 4–5 per cent of the originally available radioactive carbon was retained by the root tissues of the barley plants. Further analysis of these treated roots confirmed that the absorbed carbon was present chiefly as reduced carbon in the tissues. About 4 per cent of the radioactive carbon was present as carbonic acid while only a small, although significant, amount of the absorbed carbon was exuded at the cut end of the plants. Thus they traced the uptake of carbon by the roots but they did not determine the compounds formed after the fixation of carbon owing to the short half-life of the tracer and to the absence at that time of a convenient and rapid micro-method of separation.

The investigators in the forties did not neglect to find out whether carbon dioxide has got any toxic effect on the roots when applied in excess. Cannon<sup>40</sup> found that the growth of many roots was checked promptly by 25 per cent of carbon dioxide, but willow roots grew in 45 per cent carbon dioxide with oxygen normal or high. Seifriz<sup>41</sup> observed that 10 per cent carbon dioxide was minimum for narcosis and 25 per cent gave a rapid reaction. Valmis and Davis<sup>42</sup> reported that 20 to 30 per cent of carbon dioxide even with 70 to 80 per cent oxygen was rapidly toxic to barley. These figures suggest that carbon dioxide concentrations below 10 per cent in the soil gases are probably not highly toxic, but that concentrations above 15 to 20 per cent may be toxic to some plants. However, in the soil the

ratio between carbon dioxide and oxygen concentrations<sup>43</sup> rarely falls below 1:20 so that toxic effects of carbon dioxide under normal agricultural conditions are not very likely. One interesting thing which needs to be mentioned here is the importance of keeping the ratio between the two gases at a safe level in the solution culture experiments. Recent investigators ignore this and as a consequence their results tend to point in the opposite direction as compared with the soil culture experiments mentioned before.

The findings of Chang and Loomis<sup>44</sup> give support to the above statement. The rate of water absorption by the roots of wheat, maize, and rice growing in water cultures was reduced to 50 per cent by bubbling carbon dioxide through the solution for ten minutes in every hour. Bubbling air and nitrogen increased water absorption by 9 and 13 per cent respectively. They also found that carbon dioxide treatments reduced the absorption of the five nutrients in the order  $K > N > P > Ca > Mg$ . They attributed this toxic effect of carbon dioxide to its specific ability to change the internal pH of cells and to form hydrogen bond compounds with protein. However, it has been proved more recently that  $HCO_3$  and carbon dioxide fixation results in higher uptake of cations.

Leonard and Pinckand<sup>45</sup> concluded that root elongation was optimum with 7.5 and 21 per cent oxygen when carbon dioxide was constant at 10 per cent in the nutrient solution. Root growth was reduced at the concentration of 45 per cent carbon dioxide and was prevented completely at 60 per cent. Shoot growth appeared to be unaffected both in height and fresh weight from 0 to 30 per cent carbon dioxide, reduced at 45 per cent and stopped at 60 per cent and above.

Hammond et al<sup>46</sup> came to the conclusion that plant roots are surprisingly tolerant of reduced oxygen and high carbon dioxide pressures. They observed that carbon dioxide may reduce both root growth and the rate of potash and water absorption by unit root surfaces. The levels required however are high e.g. 5 per cent carbon dioxide in equilibrium with soil moisture when oxygen is less than 1 per cent and 20 per cent carbon dioxide with 20 per cent oxygen. Such high concentrations of carbon dioxide are rare under normal field conditions. It is quite evident that the toxic effect of this gas is due more to oxygen deficiency than to its direct effect on the protoplasm.

Borasio<sup>47</sup> has stressed the importance of carbon nutrition by stating that its assimilation by rice is respectively 40, 164, 52 and 308 times that for N, P, K and Ca. He worked with various organic manures

and supplemented manures containing ammonia, calcium cyanamide, urea, ammonium sulphate, phosphate, etc., and concluded that atmospheric carbon which is assimilated by the leaves should be supplemented by organic carbon in the form of fertilizers which will be utilized through the roots.

In the fifties, reports have been published suggesting that the bicarbonate ion is one of the contributing factors in plant chlorosis which is commonly noted in soils rich in limestone. Harley and Linder<sup>48</sup> noted that chlorosis in certain apple and pear orchards was related to the bicarbonate concentration of the irrigation water. Gaugh and Wadleigh<sup>49</sup> using nutrient cultures containing 12 me/lit. of sodium bicarbonate found that it is possible to induce chlorosis in Dallis grass but they failed to do so in the case of Rhodes grass. Later Wadleigh and Brown<sup>50,51</sup> succeeded in inducing chlorosis in dwarf red kidney beans and garden beets, by adding respectively 16 and 32 me/lit of sodium bicarbonate. Lindsay and Thorne<sup>52</sup> also induced chlorosis in susceptible plants by increasing the level of bicarbonate in the growth medium. They found that a combination of high pH and high bicarbonate ion concentration had not prevented iron absorption but apparently had resulted in the inactivation of iron within the plants. They also observed that nutrient solutions containing high bicarbonate ion concentrations increased the accumulations of iron in the roots of Great Northern bean plants, but decreased the translocation to leaves and stems.

Porter and Thorne<sup>53</sup> have found that high bicarbonate ion concentration decreases growth and chlorophyll contents of bean and tomato plants. They suggested that inactivation of the iron in plants due to the presence of large amounts of bicarbonate causes chlorosis.

Miller and Thorne<sup>54</sup> found that bicarbonate ions have an effect on the respiration of the chlorosis susceptible species whereas it had no effect on the species which were resistant to chlorosis. They noted that the apical sections of bean roots took up oxygen at nearly uniform rates when immersed in nutrient solutions which varied in pH over the range 4.5–8.5. At pH 3 and 10.5 there was a considerable reduction in the rate of respiration. In the Hoagland solution, bicarbonate ions inhibited respiration markedly and this effect increased with time. The rate of oxygen consumption by chlorosis-susceptible plants was markedly reduced by the presence of bicarbonate ions whereas resistant plants were only very slightly affected by bicarbonates.

The reports of several workers<sup>55–59</sup> suggest that a reduction in iron in the shoots of plants and, in some

cases, a reduction in cytochrome oxidase activity takes place in the presence of bicarbonate ions. Miller and Thorne thought that if bicarbonate ions affect the cytochrome oxidase system, differences in the susceptibility to chlorosis would be explained. They concluded, however, that inhibition of respiration of excised roots by bicarbonate is not explained fully by a direct inhibition of the cytochrome system.

Iljin<sup>60-63</sup> pointed out that chlorotic plants usually contain more citric and malic acid than normal plants. However, Dekock and Morrison<sup>64</sup> found that the organic acid content of chlorotic plants was often similar whether the chlorosis was produced by genetic effects, by lime or by simple iron-deficiency.

It has already been reported that the primary products of dark fixation of carbon dioxide by roots were malic and aspartic acids.<sup>12</sup> Because of the similar intermediate products in both the chlorotic plants and during the dark fixation of carbon dioxide it seems probable that the dark fixation process could be involved in these disorders. There also seems to exist relationship between the capability of plants to fix bicarbonates and their susceptibility to chlorosis. Stolwijk and Thimman<sup>101</sup> found that monocots were less capable of fixing carbon dioxide in the roots than the dicots. Brown<sup>65</sup> found that barley which fixed relatively smaller amounts of  $\text{HCO}_3$  was resistant to chlorosis, whereas, Bedri et al<sup>66</sup> noted that the chlorosis susceptible PI soyabeans fixed bicarbonate from nutrient solution at greater rates than did the non-susceptible soyabeans. These two observations confirm the above statement.

Reuther and Crawford<sup>67,68</sup> have confirmed that carbon dioxide in the soil is not a contributing factor in chlorosis because the carbon dioxide content of the soil is lowest when chlorosis is severe. They increased the concentration of the carbon dioxide by applying farmyard manure and concluded that probably soil aeration was not involved in chlorosis.

Russel<sup>69</sup> succeeded in controlling chlorosis by the application of farm yard manure and compost to the soil. This can be explained by the fact that the roots are dependent on oxygen for carbon dioxide fixation. Bandurski<sup>70</sup> found that although PEP could be formed from all intermediates of the Krebs cycle, it could only be formed in the presence of oxygen. If Jackson's<sup>71</sup> proposed reaction for the primary fixation mechanism of carbon dioxide in roots is accepted, the control of chlorosis by the application of farm yard manure can be explained.

It has been suggested that plants suffering from iron chlorosis were rich in the organic acids and free amino

acids. Rhoads and Wallace<sup>72</sup> found that these symptoms may be attributable to dark fixation of carbon dioxide by roots, but their results indicate that roots from an iron-deficient medium fixed  $^{14}\text{CO}_2$  at a much greater rate than those from the iron-sufficient medium. Thus they explain that whereas in lime-chlorosis carbon dioxide may be fixed in roots at greater rates due to the external carbonate concentrations, perhaps enhanced by an iron deficiency, in iron deficiency chlorosis, increased fixation is due solely to iron deficiency. The net result in both cases is an increased organic acid content and similar chlorotic symptoms.

On the above basis, the above workers<sup>72</sup> have suggested a hypothesis on the possible inter-relationship between carbon dioxide fixation and the reduction of iron content of the leaves. According to Jackson's<sup>71</sup> PEP carboxylase reaction, there was one molecule of inorganic phosphorus produced for each molecule of carbon dioxide utilized. Rediske and Biddulph<sup>73</sup> showed that iron is immobile in beans if the culture solution has a pH as high as 7.0, but it is mobile at pH 4.0 in the presence of low P. The above workers<sup>71</sup> conclude "that iron taken up by roots may be precipitated with the phosphorus byproduct of carbon dioxide fixation and this may account for the increased iron in the roots and stems and a decrease in the leaves". It is therefore evident that  $\text{HCO}_3$  plays a very indirect role in causing iron chlorosis. The intensity of the chlorosis will obviously depend upon the quantity and the duration of the bicarbonate ion absorption and the stage of growth of the plants in question.

The experiments of Brown<sup>74</sup> give further evidence that the incidence of iron chlorosis in P1 variety of soyabeans was related more closely to the phosphorus concentration in the solution than to the bicarbonate. It can be explained on the same basis that iron has been inactivated internally in P1 soyabeans by the presence of excess P in the solution in addition to the P released during the fixation of  $\text{HCO}_3$  by the roots in the dark.

However, the hypothesis of Thorne et al<sup>75</sup> does not agree with the above hypothesis because they concluded that there was no evidence that high phosphorus caused a precipitation of iron in plants sufficient to cause chlorosis.

Doney et al<sup>76</sup> using *Zea mays* and *phaseolus vulgaris* varied the  $\text{HCO}_3$ , phosphorus and pH levels of the nutrient solution and sprayed iron on the leaves to study the effect of these on the translocation of iron. They found that more iron was translocated from the treated leaflet to other parts of the plant as each of the variables was increased in the nutrient medium. Where

phosphorus or pH increased, due to inactivation and precipitation of iron, the concentration of iron in the plant went down and showed a slight symptom of deficiency. The concentrations of the variables used were very high. In all cases, the precipitation of iron found in the translocating portion of the plant (the stem and the petiole) increased with increasing the concentration of each variable. The proportion reaching the roots, the apex of the trifoliate leaves and two primary leaves, was correspondingly decreased. The increased concentration of phosphorus in the nutrient solution only slightly affected the movement of iron applied to leaves, but it had a significant effect on the translocation of iron to the various sections of the plant. These observations were true for bean plants. In the case of maize plants, the increased iron uptake due to increased  $\text{HCO}_3$  phosphorus or pH was distributed throughout the entire plant.

Hale and Wallace<sup>77</sup> studied the effect of  $\text{HCO}_3$ ,  $\text{CO}_3$  and  $\text{H}_2\text{PO}_4$  ions on the distribution of iron among various parts of the plant when radioactive iron was supplied to plants in the form of iron chelate of ethylene-diamine di-hydroxyphenyl acetate in the nutrient solution. They found that  $\text{HCO}_3$  and carbon dioxide decreased iron accumulation in the roots and the tops, but there was hardly any decrease in the iron content of the leaves. They concluded that neither  $\text{HCO}_3$  nor  $\text{CO}_3$  ions impeded the translocation of the iron from the roots. They failed to find any evidence of the precipitation of iron due to the presence of phosphorus in the roots or stem in the presence of  $\text{HCO}_3$ . In acid pH, in the complete absence of  $\text{HCO}_3$  phosphorus caused precipitation of iron in the roots and a slight decrease in leaves. They concluded that pH was one of the factors increasing the effect of  $\text{HCO}_3$  in producing chlorosis.

It is therefore evident that  $\text{HCO}_3$  and carbon dioxide can cause chlorosis by their indirect effect on iron precipitation only at a very high concentration, and when their concentration in the soil is increased either by adding organic matter or by fertilizing with carbonates, vigorously growing plants, with a reasonable iron reserve, will probably fail to show any nutritional disorder under the normal field conditions.

Reinau<sup>78</sup> in 1950 presented a hypothesis that the carbon dioxide originating in the soil during the decay of organic matter, is an important factor causing heavy yields of close-standing crop. Hagen<sup>79</sup> suggested the desirability of carrying out aeration studies with plants in soil whose moisture content should be allowed to vary over the usual field range. He designed his expe-

riments to observe the effect of carbon dioxide and nitrogen gas on the rate of absorption of water by previously wilted tomato plants and found that carbon dioxide treated plants take longer to recover as compared with nitrogen treated ones. Hence he concluded that carbon dioxide has a direct effect on the plant, in addition to that caused by the removal of oxygen, but, however, agreed that exposure to carbon dioxide for a short period does not cause any permanent injury.

Kursanov et al<sup>80</sup> studied the translocation of  $^{14}\text{CO}_2$ , taken up through the roots of intact bean seedlings and found that after an exposure of 18 hours in light, most of the radioactive  $^{14}\text{C}$  was in the stems, indicating that the fixation products had been translocated upwards.

When the excised roots are used—as done by Overstreet et al and many others—the whole balance within the plant is upset. On the other hand, it is already known that transpiration can play an important role in the carbon dioxide uptake through the roots. Kursanov et al<sup>81</sup> in 1952, succeeded in tracing the fixation products of carbon dioxide in the shoots after only 15 minutes exposure. They estimated that the amount of carbon dioxide absorbed by the roots was as much as 25 per cent of that taken up from the atmosphere by the leaves. In 1953 Kuzin and Merenova<sup>82</sup> confirmed the hypotheses presented by Tiulin, Yurbitsky and Reinau regarding the uptake of carbon from the organic manures through the plant roots. They noted that 180 days old wheat plants absorbed carbon dioxide readily from the manure, particularly in the early stages, when the concentration of the gas in the soil was high, and confirmed the observation of Kursanov et al by showing that at first the  $\text{CO}_2$  fixed was transported to the stems and leaves and later it was fixed in the roots. So now it can be concluded that one of the main reasons of the better response of crop plants to organic manures than to mineral fertilizers is the carbon nutrition.

On the contrary, Bolas and Ruck<sup>83</sup> using apple root stocks found that passing carbon dioxide into the soil significantly reduced the assimilation rate of plants grown in potting compost and markedly depressed their root growth. They, however, failed to detect any direct toxic effect of the gas on the roots.

The more conclusive work on the dark fixation of  $\text{CO}_2$  by roots was carried out by Poel<sup>84</sup>. Exposing excised barley roots (from seedlings one week old, grown in tap water) to  $^{14}\text{CO}_2$  (radioactive carbon being administered as  $\text{NaH}^{14}\text{CO}_3$ ) while supported in phosphate buffer at pH 5.6, he found that the non-volatile 80 per cent ethanol-soluble products of fixation were malic, citric, aspartic and glutamic acids, aspara-

they tested the hypothesis relating to factors known to influence the rate of the enzymatic fixation of carbon dioxide and malate accumulation, resulting from carboxylation of phosphoenolpyruvate and reduction of oxaloacetate observed when roots are placed in  $\text{HCO}_3$  solutions. Malate accounted for the major part of the difference in total organic acids between the potassium bicarbonate and potassium chloride treatments, although succinate fraction also was larger as a result of potassium bicarbonate treatment.

The addition of ammonium chloride reduces potassium absorption from potassium bicarbonate much more than potassium chloride. It prevented malate and succinate accumulation, and large quantities of potassium were lost from the roots to the external solution. Large amounts of  $^{14}\text{C}$  were present in several fractions, the malate containing by far the greatest amount of radioactivity.

The influence of ammonium chloride in preventing malate accumulation would appear to occur after the initial carbon dioxide fixation. It has been shown<sup>102</sup> that carbon dioxide fixation by bean root extracts is reduced only slightly by the presence of ammonia and that amino-acids rather than malate contain the majority of the fixed carbon. They conclude that in the presence of ammonium ion, carbon dioxide was readily fixed, phosphoenolpyruvate was carboxylated, but oxaloacetate underwent transaminations as well as reduction to malate. They also pointed out the importance of  $\text{HCO}_3$  ion in the soil systems and concluded that relatively low  $\text{HCO}_3$  ion concentrations are sufficient for rapid carbon dioxide fixation, malate accumulation and potassium absorption. However, because more than 5 per cent  $\text{CO}_2$  inhibits the carboxylation of phosphoenolpyruvate<sup>103</sup>, its (or of  $\text{HCO}_3$  ion) concentration at the site of the phosphoenolpyruvate carboxylase reaction will have a regulatory role in malate production. The rate of fixation will depend on the rate of decarboxylation during respiration, the pH, the relative carbon dioxide and  $\text{HCO}_3$  ion concentrations of the bathing medium and also the concentration of calcium, magnesia and ammonia.

Jacobson<sup>98</sup> and Jacobson and Ordin<sup>104</sup> have demonstrated that when excess cation over anion accumulation takes place in plant roots, there is a synthesis of organic acids equivalent to the difference. Jackson and Coleman<sup>105</sup> have already expressed the view that  $\text{HCO}_3$  ion assimilation stimulates the accumulation of cations. They suggested that carbon dioxide fixation enhances cation absorption by producing organic acid anions. So Bhan et al<sup>106</sup> undertook the evaluation of the

relationship between carbon dioxide and  $\text{HCO}_3$  ion assimilation in roots and cation accumulation. They found that  $\text{HCO}_3$  ion increased the calcium and the total cation content of the plants but decreased phosphorus in the leaves possibly as a result of precipitation. They found that soyabeans accumulate from 2 to 3 times as much potassium as  $\text{HCO}_3$  ion. This confirms the experiment of Overstreet et al<sup>88</sup> in which they reported 3 to 6 times as much potassium as carbonic acid uptake in excised barley roots. There was little less assimilation of  $\text{HCO}_3$  ion at a pH of 7.5. They also found that roots from all plant species accumulated higher amounts of sodium from sodium bicarbonate than from sodium sulphate or sodium nitrate. Increasing  $\text{HCO}_3$  ion levels with constant potassium in media also resulted in small increases in radioactive potassium accumulation by excised rough lemon roots. It was also noted that the pH of the medium is another important factor in the accumulation of potassium and calcium within the plants. The above workers<sup>104</sup> concluded that it is very difficult to separate the effects of pH and  $\text{HCO}_3$  ion on the cation accumulation. They found that dark fixation of carbon dioxide and the consequent build up of organic acids resulted in at least a short-time increase in the cation accumulation. Pretreatment of roots with an atmosphere enriched to 5 per cent carbon dioxide resulted in a subsequent increased accumulation of labelled sodium from NaEDTA and sodium citrate solutions compared with roots pretreated with a carbon dioxide-free atmosphere, indicating that prior synthesis of organic acids may stimulate cation accumulation.

The most recent work on the assimilation of  $\text{HCO}_3$  ion by roots of different plant species has been published by Bedri et al.<sup>100</sup> On the basis that  $\text{HCO}_3$  ion and carbon dioxide are both absorbed and assimilated actively by the roots and that the process of assimilation of  $\text{HCO}_3$  ion and carbon dioxide is the same<sup>97,98,71,84</sup> - these workers used bush beans, soyabean and barley plants to study the effect of bicarbonates assimilated through the roots in solution cultures. They confirmed the previous finding<sup>84</sup> that the addition of  $\text{HCO}_3$  ion to the nutrient solution leads to an increase in the organic acid content of the roots. Bush beans (dicot) accumulated more bicarbonate than either barley or avocado (monocot), in their experiments. They also confirmed that the bush beans accumulate more organic acids in the absence of iron. Using  $^{14}\text{C}$  labelled  $\text{HCO}_3$  ion they found that the increase in the organic acid content of the roots was due to bicarbonate nutrition because  $^{14}\text{C}$  was present in large quantities in all the organic acids formed. They

confirmed the observations of Kursanov<sup>81</sup> that translocation of the absorbed  $\text{HCO}_3$  ions does take place and more activity remains in the roots as compared with the leaves and stems. They explain that this low level of C present in the leaves was due to the fact that quite a lot of the  $^{14}\text{C}$  is exchanged for ordinary carbon dioxide during the process of respiration. However, in soyabbeans the translocation was quite spectacular. They concluded from their results that barley and avocado (monocots) roots assimilate less  $\text{HCO}_3$  ion than bush beans, soyabean or trifoliate orange plants (dicots), under the same environmental conditions. Most of the  $\text{HCO}_3$  ion was present in the water-soluble fraction, mainly in the organic acid fraction. In this fraction most of the activity (57 to 80 per cent of the total) was present in the malic acid fraction. The water-insoluble fraction and the amino-acids accounted for only 10 to 25 per cent and 2 to 11 per cent respectively. They also agreed that carbon be fixed by roots of all species from an atmosphere enriched in carbon dioxide.

Huffaker<sup>107</sup> et al in a study of the role of carbonic acid in plant nutrition, thought that although carbon dioxide diffuses into roots and is subsequently fixed as organic acids, other carbonate species could be formed prior to reaction. They attempted to trace the effect on plants of various proportions of  $\text{HCO}_3$  which would be present as  $\text{CO}_2$  at different pH levels. They found that the decrease in activity with increasing pH was very highly correlated with the calculated  $\text{CO}_2$  level. They concluded that this relationship cannot be explained by a change of optimum pH for the reaction. There was ample evidence to show that carbon dioxide and not  $\text{HCO}_3$  ion was the only directly reactive form in the system. This confirms that the reaction catalysed by PEP carboxylase uses carbon dioxide rather than  $\text{HCO}_3$  ion as substrate. They noticed less toxicity for  $\text{HCO}_3$  ion than for carbon dioxide.

Millar<sup>108</sup> in his recent (1960) review has referred to Jackson and Coleman's<sup>102</sup> work regarding the free absorption of carbon dioxide by roots and its active metabolism. He thinks that once the carbon dioxide is inside the plant it diffuses quickly, even quicker than water, into the cells.

Regarding bicarbonate nutrition, he cited the work of Jackson and Coleman<sup>102</sup> and Rhodes<sup>109</sup> to provide evidence that a pronounced accumulation of bicarbonate-derived carbon does take place inside the plant system. Regarding the mechanism of bicarbonate uptake he believes that it penetrates as bicarbonate salt molecules and not as ions. However, it has already been established that the mechanism of  $\text{HCO}_3$  ion fixation

is identical with that of carbon dioxide fixation by the roots<sup>97,98,71,81,101</sup>. Millar<sup>108</sup> also agreed that plants growing in a medium containing high concentrations of carbon dioxide or  $\text{HCO}_3$  ion may absorb and translocate high levels of carbon throughout the plant.

### Conclusion:

From the review the following can be concluded:

- (1) There is plenty of evidence to prove that carbon is taken up through the roots and actively metabolised inside the plant.
- (2) Both carbon dioxide and  $\text{HCO}_3$  ion can be fixed by the roots in the dark and they have the same mechanism of fixation.
- (3) The carbon which is assimilated by the roots is translocated to the rest of the plant system, with transpiration playing an important role in the transport of the fixed carbon.
- (4) The majority of investigations favour the view that this extra carbon is beneficial for plant growth.
- (5) Carbon dioxide fertilization is most effective when applied at those stages of growth when the rate of accumulation of organic substances in the plant is greatest.
- (6) Carbon fertilization results in high carbohydrate yield. In the presence of ample ammonium-nitrogen, carbon also participates in producing proteins.
- (7) An antagonistic relationship seems to exist between carbon and nitrogen because carbon accelerates reproductive growth whereas excess nitrogen delays it.
- (8)  $\text{CO}_2$  or  $\text{HCO}_3$  fixation is followed by higher cation uptake.
- (9) Chlorosis is probably a result of the interaction between pH, high  $\text{HCO}_3$  concentrations and the susceptibility of the plants.
- (10) The reaction of the rooting medium probably plays an important part in carbon nutrition.
- (11) To obtain correct information and to avoid complications due to the lowering in the oxygen concentration of the rooting medium it is preferable in experiments of this kind to use a soil or sand culture having free and normal aeration because carbon dioxide uptake through the roots is an aerobic process.
- (12) Extra carbon can be supplied to the plants by the use of organic manures, green manures and carbohydrates.
- (13) Soil carbonates also can supply some extra carbon to the plants.

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# Technical Digests

## Fertilizer Requirement During IV Plan\*

One important factor for developing our national economy is the planned increase in agricultural products to provide food and clothing to our ever-increasing population. The agricultural efforts during the Third Plan aim at national self-sufficiency in foodgrains and stepping up the production of cash and plantation crops in order to put the agriculture-based economy on a self-sustaining footing. Accordingly, targets of increase in foodgrains production have been fixed at 30 per cent and other crops at 31 per cent. To achieve such a rate of growth, intensive efforts have to be made in several directions, above all in stepping up the consumption of chemical fertilizers. Tables 1 and 2 give the targets of agricultural production and corresponding agricultural programme of the Third Plan.

TABLE 1—TARGETS OF AGRICULTURAL PRODUCTION

Commodity		II Plan	III Plan	IV Plan (Suggested)
1. Foodgrains				
(a) Rice	mill. tonnes	32	45	55
(b) Wheat	"	10	15	19
(c) Other Cereals	"	22	23	19
(d) Pulses	"	12	17	25
Total	"	76	100	120
2. Oil Seeds	"	7.1	9.8	12 (7 ground-nut & 5 other seeds)
3. Sugarcane	"	8.0	10.0	12
4. Cotton	mill. bales	5.1	7.0	9
5. Jute	"	4.0	6.2	8
6. Coconut	mill. nuts	4,500	5,275	6,000
7. Tea	mill. lbs.	725	900	1,120
8. Coffee	tonnes	48,000	80,000	100,000
9. Tobacco	"	300,000	325,000	350,000
10. Potato	mill. tonnes	3.0	4.0	5.0

\* An Assessment of Fertilizer Requirements for the Fourth Five Year Plan, P & D Div., F.C.I. Ltd., May 11, 1963

TABLE 2—AGRICULTURAL PROGRAMME OF THIRD PLAN

Programme	Unit	Target
1. Irrigation		
(i) Major & medium irrigation (gross)	mill. acres	12.8
(ii) Minor irrigation (gross)	"	12.8
(a) Agriculture	"	9.5
(b) Community Development	"	3.3
Total		25.6
2. Soil Conservation, Land Reclamation, etc.		
(a) Soil Conservation on Agricultural Lands	"	11.0
(b) Dry Farming	"	22.0
(c) Land Reclamation	"	3.6
(d) Reclamation of saline and <i>usar</i> lands	"	0.2
3. Additional Area Under Improved Seeds—Foodgrains	"	148.0
4. Consumption of Chemical Fertilizers		
(a) Nitrogenous (N)	thousand tons	1000
(b) Phosphatic (P <sub>2</sub> O <sub>5</sub> )	"	400
(c) Potassic (K <sub>2</sub> O)	"	200
5. Organic & Green Manuring		
(a) Urban Compost	mill. tons	5.0
(b) Rural Compost	"	150.0
(c) Green Manuring	mill. acres	41.0
6. Plant Protection	"	50.0

It has been estimated that per capita consumption of foodgrains will rise from 16 oz. at the beginning of the Third Plan to 17.5 oz. at the end of the said Plan. For assessing the requirement of fertilizers at the end of the Fourth Plan, the following factors are to be taken into account: (i) probable per capita consumption of foodgrains, (ii) population of the country by 1970-71, (iii) pattern of agricultural production to satisfy the varying needs of the people and to sustain the agriculture-based industrial economy of the country. A tentative target of agricultural production during the Fourth Plan may thus be drawn (last column, Table 1).

A study of the targets shows that the amount of increase in foodgrains and other cash crops production during the Fourth Plan is almost at par with that in the Third Plan period. Hence to achieve the targets of the Fourth Plan, the agricultural efforts initiated during the Third Plan will have to be doubled during

this Plan. Accordingly, the additional fertilizer capacity to be developed during this Plan would be as follows:

Nitrogenous Fertilizers as N	0.770 million tons
Phosphatic Fertilizers as $P_2O_5$	0.330 million tons
Potassic Fertilizers as $K_2O$	0.175 million tons

The above deduction suffers from one limitation. It takes for granted that consumption levels of fertilizers formulated for the Third Plan are by themselves adequate to sustain in subsequent years the production levels expected to be attained during the later years of the Third Plan period. The Agricultural programme of the Third Plan shows that only about one-third of the total agricultural production may be achieved by the consumption of fertilizers as envisaged. If the agricultural production targets were to be achieved by the application of fertilizers alone the requirements of the latter would have been as follows (Table 3):

TABLE 3—ESTIMATED FERTILIZER REQUIREMENT FOR THE ADDITIONAL PRODUCTION AT THE END OF THIRD PLAN, MILLION TONS

Commodity	Base level production 1960-61	Estimated additional production 1965-66	Estimate of fertilizer requirement		
			N	P	K
1. Foodgrains	76	24			
(a) Rice	32	13	0.80	0.40	0.20
(b) Wheat	10	5	0.33	0.19	0.08
(c) Other cereals	22	1	0.06	0.03	0.01
(d) Pulses	12	5	0.26	0.26	0.06
			(on the basis of application of 10 lbs. N & $P_2O_5$ each per acre)		
2. Oil Seeds	7.1	2.7	—	—	—
(a) Ground Nut	5.0	1.5	0.06	0.11	0.07
(b) Cotton Seeds & other	2.1	1.2	—	—	—
3. Sugarcane	8.0	2.0	0.34	0.23	0.03
4. Cotton (m. bales)	5.1	1.9	0.13	0.24	0.03
5. Jute (m. bales)	4.0	2.2	0.18	0.02	0.01
6. Coconut (m. nuts)	4500	775	0.04	0.04	0.08
7. Tobacco (thousand tons)	300	25	0.03	0.02	0.01
8. Tea (m. lbs.)	725	175	0.04	0.01	
9. Coffee (thousand tons)	48	32	(as per demand of Planters Association)		
10. Rubber	26.5	18.6			
Total			2.27	1.35	0.58

The requirements as deduced may be considered absolute. For fulfilling these, provisions for the following have been made:

(a) Chemical Fertilizers	
Nitrogenous as N	0.77 million tons

Phosphatic as $P_2O_5$	0.33 million tons
Potassic as $K_2O$	0.175 „ „
(b) Green Manure as N	0.3 „ „
(c) Urban & Rural Compost	
as N	0.35 „ „
as $P_2O_5$	0.21 „ „
as $K_2O$	0.35 „ „

This leaves an unbridged gap of: N 0.85,  $P_2O_5$  0.81 and  $K_2O$  0.055 m.tons.

The above gap in the levels of consumption of chemical fertilizers and organic manures has, however, been made up by other agricultural efforts in the following lines, viz. irrigation, soil conservation and dry farming, plant protection and pest control, good and hybrid seed distribution and improved agricultural techniques. These measures, however, can register increased yields only transitionally and represent best means which would add to production at the cost of soil fertility. Very often bumper harvests have been followed by recession in subsequent years. It is also a fact that irrigated land requires double the amount of fertilizer than the rainfed land for the same yield. Good and hybrid seeds in the absence of fertilizers give poorer yield than the acclimatised ordinary seeds.

While formulating the requirement of the Fourth Plan, one must therefore guard against the danger of a decline in the production level estimated to be attained at the end of the Third Plan in the years that follow. Therefore, production of fertilizers equivalent to that unbridged gap in the consumption levels in the Third Plan and made up by other agricultural practices should also find a place in the Fourth Plan. Based on the considerations enumerated above, the requirements of fertilizers during the Fourth Plan may be assessed as follows (Table 4):

TABLE 4—FERTILIZER REQUIREMENT IN THE FOURTH PLAN (1970-71), MILLION TONS

Fertilizer requirement	Nitrogenous as Nitrogen	Phosphatic as $P_2O_5$	Potassic as $K_2O$
1. Consumption level at the end year of the 3rd Plan	1.00	0.40	0.20
2. Additional requirement to stabilise the gain of the Third Plan	0.85	0.81	0.05
3. Additional requirement for increased food consumption due to growth of population and higher demand*	0.75	0.37	0.175
	2.60	1.58	0.425

\* In accordance with the target of agricultural programme for the Third Plan

## Methanol Plant at Trombay

The manufacture of methanol in India was first attempted by the Mysore Iron and Steel Works on a limited scale. According to Statistics on Industrial Development issued by the Development Wing, Union Ministry of Commerce & Industry in 1962, about 600 tons of methanol were consumed in India during 1960, while domestic production was only about 15 tons. The annual demand for methanol would be about 25,000 tons by 1965-66 for consumption in the following pattern (in thousand tons): formaldehyde 15.0, chemicals and drugs 3.5, polymethyl methacrylate 1.5, methylene chloride and other chloromethanes 1.5, aircraft fuel 1.5, and denaturant and solvent 2.0. The Petrochemicals Committee (1963) considered that it would be desirable to set up two new units, each with 60 tons/day capacity near the main consuming centres viz. Calcutta and Bombay, and in order to ensure low cost production the raw material viz. synthesis gas, may be obtained from refinery gas or from surplus coke oven gas through simultaneous production of ammonia and methanol.

At the instance of the Union Ministry of Steel and Heavy Industries and the Development Wing, a techno-economic survey on the possibilities of manufacture of methanol at Trombay along with a town gas plant was carried out by the Planning & Development Division of the FCI Ltd. Based on this survey, a project report\* for a 100 tons/day methanol plant using either

\* Project Report and Estimates for Methanol Plant at Trombay Division of F. C. I., P & D Division, FCI Ltd., Oct. 1963.

petroleum naphtha or refinery gas has been submitted. Since none of the adjoining refineries, viz. Burmah-Shell or Esso, are in a position to supply the requirement of refinery gas for methanol, the equivalent amount has to be obtained from the allocation of the refinery gas to be supplied by the Burmah-Shell for the ammonia plant. The refinery gas so diverted to the methanol plant would be replaced by naphtha in the ammonia plant. The processing cost of methanol production from refinery gas is cheaper than while using naphtha as feedstock (Fig. 1).

The proposed plant is claimed to be capable of processing either petroleum naphtha or refinery gas as primary feedstock. The liquid hydrocarbon is pumped to a pressure of about 15 Kg/cm<sup>2</sup> and vaporized in the presence of hydrogen, which is obtained by treating process gas from the reformer furnace and recycling it. The hydrogen-hydrocarbon gas mixture from a vaporizer flows to the desulphurization unit and is preheated by heat-exchange and a direct-fired heater to about 370°C. Any unsaturated hydrocarbons present are catalytically reacted with hydrogen to form saturated compounds, which are more stable and less apt to form carbon in the subsequent reforming operation. The same equipment also serves to convert catalytically the sulphur compounds present in the naphtha to hydrogen sulphide, which is then removed from the gas stream by reaction with metal oxides.

While using purified refinery gas as feedstock, the same is mixed with a small amount of recycled hydrogen

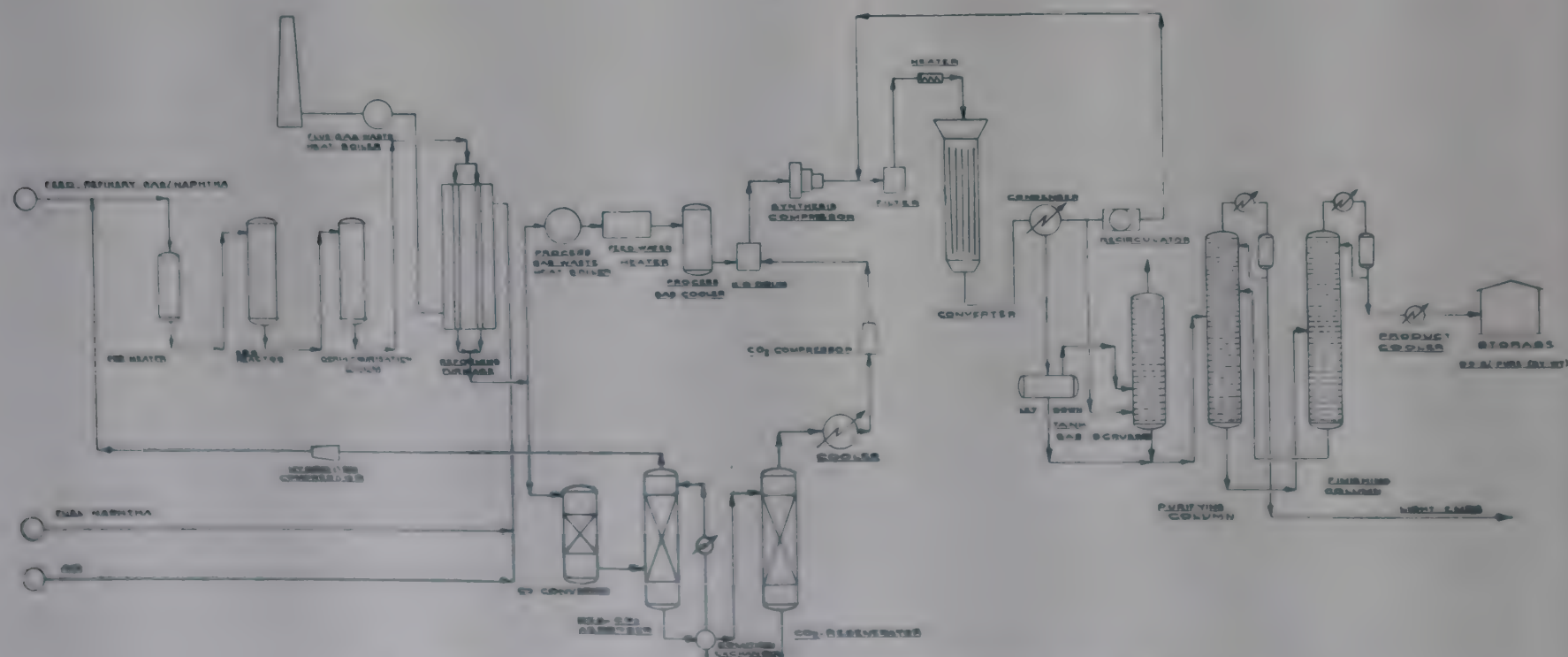


Fig. 1. Flowsheet of Manufacture of Methanol from Refinery Gas or Naphtha.

and the mixture flows through the desulphurization-hydrogenation unit.

To the purified hydrocarbon-hydrogen gas, superheated steam is added and the mixture is then introduced into the catalyst-filled tubes of the reformer furnace. Here the mixture is heated and reacted to produce a gas containing hydrogen, carbon monoxide and steam with a slight methane content at about 870°C and 12.0 Kg/cm<sup>2</sup> pressure. The heat for the reaction is supplied by the burning of naphtha/fuel oil under controlled condition outside the catalyst-filled tubes which are arranged vertically in the refractory-lined furnace.

About 94 per cent of the reformed gas flows to the reformed gas waste heat boiler at 150°C and leaves it at about 230°C and then cooled. The condensate formed during cooling is collected in the condensate separator and flows preferentially to the storage tank, from which it is pumped to the methanol purification section.

Carbon dioxide, recovered from the regeneration of an amine solution used for removing carbon dioxide from a hydrogen stream, is compressed and added to the cooled process so as to adjust its composition to that required for methanol. While using refinery gas as process hydrocarbon, an additional amount of carbon dioxide is required.

The remainder of the reformed gas is quenched with steam and condensate, and flows to the recycle converter, where carbon monoxide is reacted with steam over a catalyst producing additional hydrogen. The resulting gas, which contains about 1 per cent carbon monoxide, is quenched and cooled.

The cooled gas is scrubbed with 20 per cent monoethanolamine solution for reducing its carbon dioxide content to less than 0.1 per cent. A portion of this purified hydrogen is compressed and flows into the hydrocarbon vaporizer. The stripping steam is condensed from the reactivator by the reflux pump. The cooled carbon dioxide is scrubbed with alkaline potassium permanganate solution for amine removal, and is then compressed and added to the reformed gas to make synthesis gas of the correct composition.

When refinery gas is used as feedstock, the make-up carbon dioxide from the ammonia plant is also scrubbed with alkaline potassium permanganate solution, compressed and added to the synthesis gas.

In the direct synthesis of methanol, the mixture of hydrogen, carbon monoxide and carbon dioxide is passed over a catalyst in a high pressure converter at about 350 Kg/Cm<sup>2</sup> and 360°C, the presence of carbon dioxide being helpful in controlling the reaction. The

make-up synthesis gas and recycled synthesis gas mix and flow through a filter for the removal of compressor oil. The gas enters the converter through an annulus and then flows through a heat-exchanger and catalyst cooling tubes, being preheated to reaction temperature by heat with the converted gas. An external, direct-fired heater is provided to facilitate start-up of the converter.

The methanol formed in the converter is condensed as the converted gas is cooled by water in the methanol condenser. The crude methanol, separated from unreacted gases, flows either to the purification equipment or the crude methanol storage tank.

The purification of the crude methanol is accomplished by extractive distillation with water, using live steam. In the gas scrubber, methanol vapour is absorbed from the purge gas and this weak solution produced in the scrubber combines with crude methanol, and is pumped to the purifying column.

A loan to the Government of India has been announced recently by the U.S. Government Agency for International Development, most of which will be used to meet the foreign exchange component of the equipment for the construction of the methanol plant at Trombay by the F. C. I. Ltd. The annual rated production of the plant will be of the order of 30,000-33,000 tonne/yr. It is likely to go into production by the middle of 1965.

The price of methanol imported in bulk is of the order of Rs. 1000 per tonne while if produced indigenously it will be available at a much lower price. This will give a fillip to the methanol-based industry and save some valuable foreign exchange.

### **Desulphurization of Industrial Gases**

All industrial gases obtained from coal, coke or oil contain sulphur in inorganic and organic forms in appreciable amounts. In inorganic form, sulphur is present in the raw gases as hydrogen sulphide, and in the organic form sulphur compounds are mercaptans, carbon disulphide, thiophenes and its homologues and oxysulphides, etc. Hydrogen sulphide is the main sulphur compound in coal gas and it varies from 85 to 95 per cent of total sulphur present in the gas.

For using these gases for the synthetic chemical industry, it is desirable to remove the sulphur either partly or completely from them to prevent catalyst from poisoning or corrosion. The presence of hydrogen sulphide and other sulphur compounds in gas is also hazardous for various reasons. Hydrogen sulphide

causes drip water to be corrosive and it also corrodes the metal parts of gas metres and other equipment for handling gas. The sulphur in gas when burnt in industrial heating equipment is converted to sulphur dioxide and trioxide which pollute the atmosphere and corrode metal parts.

In all advanced countries where coal gas has an extensive use for town supply, the specification of sulphur is about 0.09 gr. of hydrogen sulphide per 100 cft. With increasing use of gas in towns of India and with growing emphasis in public health, promulgation of laws enforcing minimum hydrogen sulphide content in the gas supply is likely to be adopted in the near future. Further, with the increasing demand of fuel and synthesis gas the removal of sulphur, and often its subsequent recovery, will receive much greater attention than has been the case so far.

Even in pre-war periods quite substantial amounts of sulphur were being recovered in the western countries from coal gas, the bulk of which was being used for production of sulphuric acid and for agricultural purposes. Iron oxide purification for the removal of hydrogen sulphide has been in vogue for several decades, although there are now several more economical wet methods.

The most widely used iron oxide for removing hydrogen sulphide from gas is the bog iron ore. Since India has no deposits of bog iron ore she shall have to depend on prepared iron oxide.

A process has been developed in 1958 by the then Technological Division\* of the Sindri Fertilizers & Chemicals Ltd., the precursor of the Planning and Development Division, on the manufacture of a suitable mass consisting of hydrated iron oxide and calcium sulphate deposited on a suitable fluffing agent for dry removal of hydrogen sulphide from industrial gases.

The process is as follows: crushed ferrous sulphate heptahydrate or ferrous sulphate monohydrate and precipitated calcium carbonate in equivalent quantities are mixed with a fluffing agent, viz. wood shaving or fly ash, in a conventional mixer for 15 to 30 minutes with occasional addition of water to keep the whole mass wet. After thorough mixing of the ingredients the mass is taken out and exposed to atmosphere. All the ferrous sulphate gets gradually converted to iron carbonate by reacting with the calcium carbonate present in the mass, which is kept wet till the reaction is complete. The moist iron carbonate undergoes oxidation

and hydrolysis due to exposure to atmosphere. The process of complete conversion of ferrous sulphate to iron carbonate and subsequent oxidation and hydrolysis can also be carried out in a closed chamber with injection of air in it. The whole of the iron in the blend gets gradually converted to hydrated iron oxide making the product ready for direct charge in the purifier boxes employed for removal of hydrogen sulphide from industrial gases.

The rate of reaction between the calcium carbonate and ferrous sulphate depends on the particle size of the reactants and on the nature of the calcium carbonate.

### **Ion-Exchanger from Acid Sludge**

The phenomenon of ion-exchange is the exchange of ions occurring on contacting an ionic solid with an electrolytic solution. It emerged as an industrial tool at the beginning of the 20th century, when the use of natural and synthetic siliceous exchangers for water-softening was the first major attempt to utilize ion-exchange on a commercial basis, and this continues even now to be one of the major applications of ion-exchange. In this application, the hardness-producing ions of water supplies are removed and exchanged from sodium ions by passage through a column of cation-exchanger that has been regenerated with brine. Since the discovery of certain synthetic resins capable of exchanging ions quickly by Adam and Holmes in 1935, ion-exchange resins are gradually replacing the older inorganic synthetic and the naturally occurring zeolites.

In view of the improved stability of the cation-exchangers as well as various anion-exchange materials capable of removing acids from solutions, the application of cation-exchanger in hydrogen cycle has been in wide practice for complete deionization of water, purification of sugar and glycerine solutions, treatment of trade effluents, recovery of precious materials from electroplating wastes, concentration of uranium salts, etc.

A process<sup>1</sup> has been developed in the Technological Wing of the Planning & Development Division, F. C. I. Ltd., on the preparation of an ion-exchange material from acid sludge obtained as a black viscous, evil-smelling liquid during acid washing of crude benzol in the byproduct recovery units of coke oven plant. The high acid content and the peculiar nature of the sludge make its disposal extremely difficult, while by this

\* 'Process of Manufacture of a New Synthetic Desulphurization Mass', Indian Pat. No. 61247 (Inventors: Dr. K. R. Chakravorty, S. P. Sen and K. K. Ghosal)

<sup>1</sup> Process for Preparation of Ion-exchange Material from the Acid-Sludge of the Coke Oven Byproduct Recovery Plant (Inventors: Dr. K. R. Chakravorty & B. K. Dutta—Indian Pat. No. 62697; Belgian Pat. No. 589620; Canadian Pat. No. 647981)

process the problem of disposal is eliminated completely yielding in addition a highly valuable material of industrial use.

The preparation of the cation-exchanger resin<sup>1</sup> consists of digestion of the acid sludge at 100-150°C, when the mass solidifies. The mass is crushed and washed with water and then with a dilute alkali. On treatment with a common salt solution, the mass is converted to a sodium salt. The operating capacity of this cation-exchanger is of the order of 8-15 kgs/cft.

An improvement<sup>2</sup> on this process has been made to produce a resin of higher stability and exchange capacity. In this process a further quantity of the acid is added during digestion and the solid mass thus obtained is cured for a longer time at 100-200°C. The improved resin is stable even at higher pH and temperature. It has a salt-splitting capacity of 15 kilograms of calcium carbonate per cubic foot and a total exchange-capacity of 28 kilograms of calcium carbonate per cubic foot of wet material.

This resin<sup>2</sup> has been in use for water purification at the Sindri Unit of the F. C. I. Ltd. giving satisfactory performance.

### Beneficiation of Rajasthan Gypsum

The present annual requirement of gypsum at Sindri Unit of the Fertilizer Corporation of India Ltd. for the manufacture of ammonium sulphate is of the order of 7.5 lakhs tons. One of the serious problems Sindri has had to face over the years has been the dwindling reserves of the fertilizer-grade gypsum (with above 85 per cent gypsum content) which has sometimes forced the Unit to operate its sulphate plant with material of about 80 per cent purity gypsum causing difficulties such as increased loss of ammonium sulphate with the sludge, and greater wear and tear of the equipment because of increased production of sludge. Meanwhile, efforts have not been spared to look out for newer sources of gypsum of acceptable quality. The sources located, however, are scattered over wide areas and situated far away from railheads. Meanwhile, it has been decided to convert a portion of the sulphate plant to direct neutralization (by sulphuric acid) process by the end of 1965, to relieve the demand on gypsum by about 5.79 lakh tons.

At the instance of the Board of the Fertilizer Corporation of India Ltd., studies were, therefore, undertaken

by the Planning & Development Division\* for beneficiating lower grade gypsum available from easily accessible areas. Deposits of gypsum are scattered over a large area in each group of mines, viz. Kavas, Bikaner and Nagaur groups, but in many of the places the mined gypsum has to be transported over long distances by truck to the nearest railway station. For these reasons, no suitable central site could be selected in the mine area for locating the beneficiation plant. Consideration was given to the feasibility of setting up a beneficiation plant at Agra, where currently most of the gypsum from the metre-gauge is transhipped to the broad-gauge wagons for despatch to Sindri. Alternatively, the advantages of having a plant at Sindri itself has also been assessed.

For carrying out the beneficiation, there are several processes, both dry as well as wet, which have been considered (Table 1). Among the three dry beneficiation processes examined one had been developed by the National Metallurgical Laboratory, Jamshedpur, and a second one had been evolved in this Division while the third is a modification—suggested by this Division—of the existing gypsum grinding section at Sindri.

In the dry process developed here, the raw gypsum was proposed to be screened directly in several stages on separating out the —60 mesh (B.S.) portion, which involves a rejection of about 20 per cent of the material. It was observed that the purity of the material for use could be upgraded by 3.5 per cent.

In the process developed by the N.M.L., the raw gypsum is crushed to —8 mesh size and screened in two parallel streams to separate the —100 mesh portion as rejects, the latter constitutes about 17 per cent of the total gypsum, and by its rejection the purity of the residual gypsum improves by 8 per cent. In calculating the process economics of beneficiation for supply to Sindri, the location of the beneficiation unit is quite a critical consideration. Considering from this aspect, Sindri appears to be the most suitable site, where the existing wagon tippers, grinding mills, storage sheds and conveying systems can be utilized, thus saving considerable amount of the capital expenditure on equipment. On the other hand, the location of the unit at Sindri does not save transport charges for hauling the dross associated with gypsum all the way from Rajasthan to Sindri. The existing grinding mills at Sindri can be modified suitably to crush the gypsum to —8 mesh size. If beneficiation is done in Rajasthan,

<sup>1</sup> Improved Cation Exchangers from Acid Sludge of Coke Oven Plant, Indian Pat. No. 80211 (Inventors: A. C. Nanda, B. K. Dutta & Dr. K. R. Chakravorty).

\* 'A Study on Beneficiation Measures for Improving the Quality of Gypsum from Rajasthan Mines', P & D Division, F. C. I. Ltd., Jan. 1964

TABLE 1—SUMMARY OF THE DIFFERENT SCHEMES OF BENEFICATION

Sl. No.	Process	Amount of raw gypsum to be handled and purity (% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), lakh ton	Amount of product gypsum & purity (% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), lakh ton	Amount of treated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced, lakh ton	Cost per ton of treated gypsum, Rs.	Cost per ton of treated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Rs.	Capital investment		Remarks
							Foreign Exchange, Rs. lakhs	Indian currency, Rs. lakhs	
1.	Dry beneficiation No. 1 (Installed at Agra)	7.0 (82.0%)	5.6 (85.5%)	4.78	58.8	68.70	11.0	28.5	Final purity is not satisfactory for efficient running of plant.
2.	Dry beneficiation (No. 2)	6.5 (82.0%)	5.38 (89.0%)	4.78	63.70	71.6	5.75	7.5	Final purity is good from the operational point of view of the plant.
3.	Dry beneficiation (No. 3)	5.82 (82.0%)	5.67 (84.5%)	4.78	53.50	63.45		2.50	Final purity is not satisfactory.
4.	Wet process (Washing and classification)	6.25 (82.0%)	5.32 (90.0%)	4.78	70.30	77.9	16.75	29.75	Final purity is very good

N.B. Existing price of gypsum at Sindri:

(a) per ton of gypsum (purity 82.0%)—Rs. 52.0

(b) per ton of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  —Rs. 63.4

the upgraded gypsum of size  $-8+100$  mesh, has to be bagged before despatching to Sindri. This will obviously increase the cost in case the beneficiation plant is established say at Agra or in the gypsum mining area.

The wet beneficiation process will comprise a washing plant consisting of a Hardinge type tumbling scrubber with a Trommel 1/4 inch rotating screen and a two-stage Dorr classifier. But if this process be adopted, Sindri will be a better location.

The present sources of the fertilizer grade gypsum are not expected to feed the Sindri works for many more years. Recently a large gypsum deposit has been located by the Geological Survey of India near Nagaur town in Rajasthan; material having a purity of 85-88 per cent can be extracted from these reserves which are estimated at about 800 million tons at depth between 50 and 100 metres. Of course, the winning of the mineral from such a depth will add to the cost of the gypsum by about Rs. 4.00 per ton or even more, because of the highly specialized technique of shield mining which shall have to be adopted. However, before taking any decision either in favour of beneficiating the lower grade gypsum or on the underground mining of Nagaur deposits, many other points having a bearing on the production economics of ammonium sulphate manufacture at Sindri shall have to be considered.

The reserves of the present working of gypsum cannot last more than five years and even by beneficiation of the lower grade ores, the life of the present workings

can be extended by say about another span of five years. Alternatively, if the Nagaur deposits are worked, the cost of the raw material, viz. gypsum, would be fairly high, on top of which is the high cost of its transport from Rajasthan to Sindri.

The possibility of changing over the production pattern of ammonium sulphate at Sindri to base it to sulphur from the pyrites at Amjhore, near Dalmianagar (Bihar), deserves consideration for adoption. One of the alternatives considered is to replace the present gypsum process by direct neutralisation of ammonia with sulphuric acid produced from sulphur.

Another alternative suggested is the manufacture of phosphoric acid from rock phosphate by sulphuric acid treatment at Sindri yielding calcium sulphate as by-product which can substitute Rajasthan gypsum. The phosphoric acid on treatment with ammonia will also yield another important fertilizer viz. ammonium phosphate, thus improving the production and cost economics at Sindri. This will reduce strain on the railways by cutting down the ton-kilometre movement of the raw material to Sindri by about ninety per cent. The Development Council has examined this scheme and found the feasibility of changing over to the byproduct sulphate process. The Board has now agreed to the discontinuance of the manufacture of ammonium sulphate from Rajasthan gypsum at Sindri as early as practicable. Hence further work on the beneficiation of Rajasthan gypsum has been discontinued.

# Notes & News

## World Fertilizer Market

The causes for the wide and increasing disparity in agricultural production and levels of nutrition among different countries are many and include economic, technological, institutional and cultural factors. Considering the technological factor, Coleman has estimated that world fertilizer consumption in 1970 will be 48.5 million tons of nutrients as compared to 27.1 m. tons in 1959-60, while Ewell estimates additional world fertilizer requirements at 40 pounds of nutrients per capita for whose production the capital investment required would be \$ 21 billion during the next 10 years. Considering past trends, it is observed that fertilizer consumption increased from 7.5 million in 1945 to 28.5 million tons in 1960-61, and the increase was divided between the developed and less-developed countries on an approximate 10 : 1 ratio. In the developing countries, the rapid increase was limited to a few countries in some regions, and in some associated with the increased production of cash and export crops.

For considering an estimate of fertilizer requirements in 1980, one has to determine the effective future demand for food which is based on the following factors, viz., population growth and rate of economic development. Cochrane et al estimate the demand for food in the developing countries will increase at an average annual rate of 3.48 per cent compounded per year during 1960-75. About 40 per cent of this increase will be due to greater per capita consumption associated with an increase in national income at an assumed rate of 4-5 per cent per year, and the balance (60 per cent) will be due to population, while Sukhatme estimates that the world's food supply would have to be doubled by 1980 if reasonably adequate levels of nutrition are to be met.

Williams and Couston have developed a relationship (in a parabolic curve) between the national average yield of all crops and the use of fertilizer ( $N + P_2O_5 + K_2O$  Kg/Hectare) for 41 countries, and a

value index of crop production. Their data provide a useful basis for estimating the amount of fertilizer any country may need in order to attain a desired level of productivity per unit of arable land. Using this method and assuming that 75 per cent of the increased food and agricultural production required in 1980 will come from increased yields, Parker has estimated the 1980 fertilizer requirements.

If the required level of fertilizer consumption in 1980 were to be attained, world consumption would have to increase at an average rate of 4.7 per cent per year, which is possible since this rate is only two-thirds of the rate of increase for 1950-60.

In the developing countries, the urgency to increase agricultural production is great, and a recent survey by FAO indicates that most countries plan an annual increase in agricultural output of 4 to 6 per cent per year. In 1963 the U.S. Agency for International Development made an operational survey of factors associated with increasing fertilizer consumption in developing countries which indicated the following: (i)

a fair to good crop response to moderate amounts of fertilizers, the percentage increase varying from 15 to more than 100 with an overall figure of 86. The increase in crop produce per pound of plant nutrients ranged from 1 to more than 40 lb with an average of 17 lb for grain and 13 lb for all crops. (ii) The use of moderate rates of fertilizers is profitable on nearly all food crops in all countries at current prices for fertilizers and crops. The return per dollar invested in fertilizer was generally ranging from 1 to 6 dollars. (iii) 1980 fertilizer requirements will be 23 per cent higher than the estimate made from the FAO curve on crop yield and fertilizer use. This would indicate a requirement of about 37 million tons of nutrients in the developing countries in 1980. (iv) Emphasis should be laid on (a) fertilizer use combined with the use of better cultural practices, good seed, pest control and other soil, water and crop management practices, (b) correlation of soil analyses with field test data and soil surveys. (v) A high percentage of soils tested is low in nitrogen and phosphorus; potash deficiency is also widespread.

FERTILIZER CONSUMPTION IN 3 SELECTED AREAS OF WORLD

Area	1960 Consumption, mil. metric tons	Compounded Rate of Increase, %		Estimated Consump- tion, mil. metric tons	
		1960-70	1970-80	1970	1980
Western countries (including U.S., Canada, W. Europe, Japan & Oceania) ..	20.0	3.0	3.0	26.9	36.1
Eastern Europe & USSR ..	5.0	12.0	5.0	15.5	25.3
Developing Countries (including all countries of Latin America, Near East, Far East & Africa except China). ..	2.7	15.0	10.0	10.9	28.3
World .. ..	27.7	6.8	5.3	53.3	89.7

[F. W. Parker et al, Fertilizer News, 9(1964), 3, 7-15]

## Ammonia Liquor from Lurgi Plant

The high pressure coal gasification plant at Coleshill of the West Midlands Gas Board, U.K., is expected to have gone in full production. It is meant to supply more than 40 million cu. ft. of gas daily for the grid of gas minus supplying major towns in the area. Included in the ancillary plant are two units for production of 4,900 gallons of concentrated (25%) ammonia liquor (CAL) from the de-phenolated liquor from phenosolvan plant. The complete concentration plant includes two distillation units each incorporating a liquor decarbonator whereby the specific gravity of CAL is controlled and maintained below the minimum value necessary to avoid crystallization.

[Nitrogen (1963), 26, 32]

## New Catalyst Reduces Ammonia Cost

A new catalyst G-66 developed by Girdler Catalyst Department of Chemotron Corporation, Louisville, USA, for producing hydrogen from natural gas has reduced to the extent of 10-25 per cent of the plant costs. The initial cost of a typical 25 million cu. ft./day hydrogen plant, which is now close to \$ 4 m., may be reduced by as much as \$ 1 m.

Packed into a cylinder reactor vessel through which hydrogen synthesis gas is passed, the aspirin-sized catalyst pellets promote the water gas shift reaction that uses steam to convert CO to CO<sub>2</sub> to produce additional hydrogen. Use of the Catalyst G-66 allows the reaction to be carried out as low as 300° F with greater conversion to CO<sub>2</sub> than is possible at 650-800° F required by the conventional iron-chrome catalysts.

More than half the cost of hydrogen generating facilities is due to purification stages required. Using this catalyst one or more shift reactor stages can be eliminated from previous multiple designs. Part of the savings results from the simultaneous elimination of CO<sub>2</sub> removal equipment and sealing down of the methanation apparatus commonly used to eliminate remaining traces of carbon monoxide, particularly for ammonia production. The life of G.66 Catalyst in service is estimated at more than 5 years with about 200 cu. ft. charge required in the shift reactor stage of a 25 m cu. ft. per day hydrogen plant or 300 s. tons p.d. ammonia plant. It has no tendency to form coke or hydrogenate CO to methane at normal operating temperatures.

[Nitrogen (1963) 26, 46-47]

## Largest Ammonia Plant

The largest ammonia plant in the world, 1,400 tons/day capacity, is to be built by Olin in Lake Charles, U.S.A., as part of a fertilizer expansion programme costing above \$ 52 millions. The additional facilities call for a new urea plant at Lake Charles with a capacity in excess of 140,000 tons/year; a high analysis fertilizer plant (Ammono-Phos) at Joliet, Illinois with a 200,000 tons/year capacity; and added capacity at Pasadena, Texas, to increase the present capacity of high analysis fertilizer there to about 600,000 tons/year.

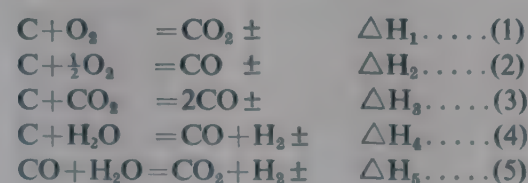
The ammonia plant will have a capacity double of the largest plants built to date.

[Chem. Engng. Prog., 60 (1964), 2, 26]

## Slagging Gasifier

The problem of utilisation of low grade non-coking coal has assumed much importance in recent times. The coals of Andhra Pradesh are of low grade having up to about 35 per cent ash. A suitable process of utilisation can be its complete gasification.

The gasification characteristics of these high ash coals from Kothagudem area (A.P.) have been studied at the Regional Research Laboratory, Hyderabad\*, in an experimental suspension-cum-fixed bed longitudinal type unit for gasifying 5-10 lbs of coal per hour at atmospheric pressure. For the investigation, a slack coal (size  $\frac{1}{2}$ -1", ash 19.2 per cent) was taken having the following ash fusion characteristics (Table 1). The oxy-steam coal gasification is expected to take place in the following sequence :



In addition to the above reactions, the following may also take place:



TABLE 1—FUSION CHARACTERISTICS OF COAL ASH

	Mildly Reducing Atmosphere
Initial Softening Point, °C	1,445
Hemi-spherical Point, °C	1,500
Fluid point, °C	1,510

Ash Analysis (%): SiO<sub>2</sub> 63.89; Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> 20.30; Fe<sub>2</sub>O<sub>3</sub> 11.38; CaO 2.14; MgO 1.33; SO<sub>3</sub> 0.75; Alkalis (by diff.) 0.21.

The various factors viz. molar relationships, material balance, adiabatic flame temperature, determination of the time of gasification, etc., for the design of an economic size of the gasifier on the basis of 1,000 lb coal/hour, 1,500°C and O<sub>2</sub>/Coal ratio of 8.0 Scft/lb have been studied.

## Small Synthetic Ammonia Plant

Some design innovations by J. F. Pritchard & Co. of Kansas, U.S.A., have enabled small units to compete economically with large plants and make the maximum use of the standard industrial parts. These developments, together with other design features, have resulted in marked cost savings in producing ammonia and may enable 60 tons/day plants to compete with 300 tons/day plants. Some of the companies offering 60 tons/day plants are concentrating on the preassembly of plant components in a drive to keep initial plant cost low, as some of the conventional ammonia plants need custom parts, which may lead to maintenance delays and replacement problems.

The most significant innovations have been in the design of synthesis gas converter. In the new design, the converter has been broken down into five vessels—a heat exchanger and four units containing catalyst. The gases were not recirculated and considerably higher pressures (about 14,000 psi), instead of 3,000-5,000 psi as in the conventional plants, were used. This eliminates the craneway and rigging, since the spent catalyst can be handled by a vacuum hose without removing the intervals. It also gives better reaction control such as simplified temperature control and elimination of hot spot. The heat exchanger, being a separate vessel, permits greater use of standard equipment, which reduces downtime, maintenance costs and spare parts inventory.

Since catalytic formation of ammonia is an exothermic reaction and the catalyst must not be overheated (and kept below 930° F), the ability to control each catalyst vessel separately by the supply of coal

\*Ramacharyulu, M., Rao, K. Seshagiri, Krishna, M. G. and Zaheer, S. H., Indian Chem. Engr., 5 (1963), 183/138.

quench gas in the new design is a great advantage.

Another feature of the Pritchard design is the use of preassembled reforming furnace. They have put much effort into unitizing the design of these plants, and controls have been centralized to cut manpower needs. Unitization has also reduced space problem. They point out that a 60-100 tpd plant at \$ 20,000-24,000 per daily ton can be supplied by them.

[Chem. & Engng. News, 41 (1963), 52, 38-39].

### New Hydrocarbon Reforming Process

The research laboratories of Office National Industrial de l'Azote (ONIA) in Toulouse, France, have developed a new tube-cracking process suitable for the conversion of a wide range of feedstocks from natural gas to naphtha with distillation end-points as high as 250°C and containing variable amounts of sulphur compounds. It can produce hydrogen-rich gases or gases intended for the synthesis of ammonia, methanol and alcohols. Special steam-reforming catalysts, efficient in operation at low temperatures having a long life, have been patented by ONIA. Steam consumption is reduced and reforming takes place without formation of carbon black. Large savings in operating and investment costs are claimed as the result of reduced plant size and power consumption, and the sulphur contents of the feedstocks are reduced to less than 1 ppm.

Using this process, known as ONIA-G1, it is claimed that it is feasible to produce under pressures up to 40 kg/cm<sup>2</sup> a gas suitable for 4,200 millitherm per cubic metre gas without enrichment. Such a gas can also be stored underground. Installation of several plants to produce town gas using this process is under consideration.

[Nitrogen, (1964), 27, 31]

### Hercules Nitric Acid Process

The Hercules process, whose key features are minimum capital investment, low maintenance costs, reliable performance, easy operation and minimum manpower requirements, has recently become available through a licence in combination with Foster Wheeler.

In this process, the oxidation of ammonia and the absorption of nitrogen oxides take place at a pressure of 8 atmos-

pheres. The process air is supplied by a centrifugal compressor discharging it at 125 psig and the compressed air is preheated. The precisely ratio-controlled hot air and ammonia mixture enters the converter where oxidation takes place on a platinum-rhodium catalyst. The oxidation gas leaving the converter consisting of nitric oxide, oxygen, nitrogen and water vapour passes through the air preheater and spent gas superheater. The partially-cooled gas then flows to the platinum filter to recover the finely divided platinum which comes off the catalyst. Final cooling of the oxidation gas to about 95 F and oxidation of nitric oxide to nitrogen dioxide take place in multi-pass cascade cooler condenser. The nitrogen dioxide and nitric acid condenser in the cooler, flow on to a tray near the bottom of the absorption tower. Intimate contact between the gases and the condensate is provided by specially designed trays which are provided with cooling coils to remove the heat of absorption and reoxidation. The acid leaving the tower is heated and then passes to a bleacher where nitrogen dioxide is stripped off by air.

Recently, the design has been further developed by Foster Wheeler Corporation and Hercules to increase the thermal efficiency of the plant. The plant may be made self-sufficient in power requirements by use of steam turbine drive for the air compressor. Acid condensate from the cascade-cooler is delivered to the absorption tower by gravity.

Practically all of the nitrogen dioxide is removed in an externally located bleacher, and acid to be bleached is heated by steam in an external corrosion-resistant preheater which minimises maintenance. Since air is not used to heat the acid to the bleaching temperature, this temperature can be minimised at the same time keeping the base of the absorption tower as cool as possible, thus increasing the absorption efficiency.

For a plant producing 57 per cent nitric acid and using cooling water at 75°F, the following average efficiencies (in percentages) have been achieved: conversion efficiency 95.5; absorption efficiency 99.0; overall efficiency 94.6; and nitrous oxide in stack gases 0.10 wt. as nitric acid.

[Nitrogen (1964), 27, 26]

### Carbon Dioxide Nutrition

Chlorophyll—the green colouring matter in plants—utilises the sun's energy and

converts carbon dioxide and water into carbohydrates. Carbon dioxide is as necessary for the process as mineral nutrients in the soils are for the growth and development of the plant.

Obviously the quantity of carbon dioxide could only be regulated under controlled conditions and the experiments conducted in glass houses in U.K., Holland and U.S.A. have demonstrated the profitability of carbon dioxide enrichment. The benefits accrue both in the direction of augmented yields and in the reduction of the maturity periods. The glass house atmosphere normally contains 0.033 per cent carbon dioxide which goes much below this level with the utilisation of the gas by the plants. A level threefold of this, viz., about 0.1 per cent, appears to give optimum results. Increase in carbon dioxide content of this order has brought about a 37 per cent weight-increase in case of lettuce crops.

Carbon dioxide content can be raised by releasing the pure gas in liquid form or by exposing solid carbon dioxide (dry ice) containers in glass house or by burning propane fuel or paraffin. It is desirable to increase the carbon dioxide content only after the plants have grown sufficient number of leaves in order that they derive full benefits. Also for optimum results, higher diurnal temperatures with a minimum of 65 to 70°F are necessary, and night temperatures may be as low as 50°F. Exceptionally high temperature is not helpful and to even it ventilation may be resorted to.

The addition of carbon dioxide has proved to be an economic proposition, and the increased yields far exceed the extra allocations needed. Besides, the reduction in maturity periods can enable farmers to raise three crops in the same time as normally required for two.

[Science Reporter, 1 (1964), 175-176]

### Imported Ammonia for Fertilizer Complex

W. R. Grace & Co. of U.S.A. have planned to market bulk ammonia on a worldwide basis. Anhydrous liquid ammonia made by a Grace affiliate at a 215,000 ton/year plant at Point Lisas, Trinidad, is shipped 2,000 miles by a 9,000 ton refrigerated tanker to Carolina Nitrogen's—a Grace subsidiary—new plant at Wilmington. The cost of ammonia (said to be less than \$ 60/ton) is \$ 10-20 cheaper than outside production would

be, because of marked difference in the cost of natural gas.

Nitrogen solutions account for 60 per cent of total output at Wilmington. The rest is sold as prilled ammonium nitrate and an ammonium nitrate-limestone mixture.

Anhydrous ammonia is stored at—28°F and 0.5 psig in a 20,000 ton tank, of dimensions 132 ft. dia., 75 ft. high, double-walled and insulated with a 30 inch thickness of expanded perlite in the annular space. Low temperature is maintained by a 200 hp two-stage refrigeration compressor and a large air-water evaporative condenser.

A high-pressure nitric acid plant produces 450 tons/day of 56 per cent product. It contains the largest single-train ammonia burner in U.S.A. plus an 11,110 hp rotary air compressor. Power is economised by mixing absorber tail gas with methane burning the mixture over a catalyst and recycling the resulting combustion gases through a turbine. Reaction of the nitric acid with the ammonia at 45 psig produces an 83 per cent ammonium nitrate solution. This is either sent to storage or concentrated to 95 per cent prior to prilling. The prill tower is 185 ft. high and operates with a series of simple shower heads.

[Chem. Engng. 71 (1964), 6, 106]

### Hydrogen from Natural Gas

Steam reforming is a widely used process for manufacturing hydrogen. A steam-reforming hydrogen plant can be divided into a hydrogen generation section and a hydrogen purification section. The natural gas (generally of 1,000 Btu at 50 psi) is compressed to 150 psi at the outlet of the primary reformer. The gas is desulphurised in activated carbon drums to safeguard the reforming catalyst and then preheated in the convection section of the reforming furnace. Steam is added in the ratio 3 to 5 moles of steam to 1 of carbon, and the mixture is reformed in catalyst filled tubes in the radiant section of the reforming furnace according to  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ . The reaction is highly endothermic and is carried out at 1,300-1,500°F. The reformed gas is cooled by direct water quench or in a waste heat boiler to 650 to 750°F and flows to a shift converter where about 90 per cent of the carbon monoxide is shifted to produce more hydrogen by the following equation:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ .

The shifted gas is then purified. The carbon dioxide is removed by absorption with monoethanolamine, Vetrocoke, or hot carbonate solution. All or most of the solution regeneration heat is obtained by exchange with the hot shifted gas stream. The remaining carbon dioxide in the hydrogen leaving the absorber varies with the process used and the operating conditions, but is normally reduced to 0.1-0.2 per cent on dry gas basis.

The small amounts of carbon oxides remaining in the hydrogen are converted to methane at 600-880°F over a catalyst. The purified hydrogen is then compressed to the required pressure.

In a paper, G. T. Lee, J. D. Leslie and H. D. Rode Kohr [Petr. Refiner, 42 (1963), 9, 125-128] have discussed the major variables affecting the present-day economics. Based on construction costs for U. S. Gulf Coast conditions a 5 MMcfd plant costs just a little over \$ 1 million, a 10 MMcfd plant a little over \$ 1.5 million, a 30 MMcfd plant almost \$ 3.5 and a 50 MMcfd about \$ 5.0 million. The costs of manufacturing hydrogen in plants with capacities 5 to 50 MMcfd and with fuel costs ranging from 20 to 50 cents per million Btu have been indicated. The natural gas feed and fuel requirements are 288 and 200 scf assuming 1,000 Btu. Steam is essentially in balance with about 3.5 lbs excess steam produced, and boiler feedwater makeup and cooling water circulation are 11.2 and 7.35 gallons. The power requirements are 2.31 Kwh. The catalysts and chemicals costs are about 0.22 cents per thousand cft of hydrogen.

With natural gas at 20 cents per million Btu, the hydrogen manufacturing costs range from 18 to about 31 cents depending on plant size. At 30 and 50 cents gas the manufacturing costs range as 23-37 and 34-47 cents respectively.

### Fertilizer Trials

The Institute of Agriculture at Anand (Gujarat) has undertaken the study of comparative performance of nitro-phosphate, ammonium sulphate phosphate and urea with current sources of fertilizers, commonly used in the country, on the yield and quantity of some common crops of Gujarat. In a tentative report [Fertilizer News, 9 (1964), 4, 16-21], results of experiments on *bajri*, *Sundhia* fodder, *jowar* and paddy grown in *kharif* or summer season covering the period May to December 1963 have been given.

The research programme consisted of 12 experiments to study the comparative effects of the above three fertilizers with and without superphosphate, on the following crops: 1 Cereals—paddy, wheat (irrigated), *kharif bajri* and hot weather *bajri*; 2. Fruit and Vegetables—banana, brinjal, and tomato; 3. Forage—*kharif sundhia jowar*, hot weather *sundhia jowar* and lucerne; 4. Non-food—tobacco and castor. All the experiments except that on paddy were conducted on the deep brown coloured sandy loam soil popularly known as 'goradu'. The experiment on paddy was carried out in 'kyari' soil which is believed to have been developed from the sandy loam soil under low-lying conditions.

The results indicated that in general there was increase in yields of grain and straw with increase in quantity of nitrogen applied. The application of  $\text{P}_2\text{O}_5$  either in the form of nitrophosphate or superphosphate did not show advantage in increasing the yield of paddy, which was probably due to the very high status of available  $\text{P}_2\text{O}_5$  (160 kg/hectare) in the soil present before sowing the crop. Nitrophosphate was in no way inferior to other sources of fertilizers when it was applied at the levels of 30 kg/hectare of nitrogen and 30 kg. of  $\text{P}_2\text{O}_5$  per hectare. However, it was somewhat inferior at a higher level i.e. at 60 kg/ha of nitrogen.

### Phosphoric Acid by Solvent Extraction

Israel Mining Industries of Haifa have patented a process of phosphoric acid manufacture involving the treatment of phosphate rock with aqueous hydrochloric acid using a flocculant to settle out the insoluble residue. This stage is followed by the extraction of phosphoric acid from the clarified liquor by means of organic solvents ( $\text{C}_4$  or  $\text{C}_5$  primary alcohol) and in the third stage the acid is reabsorbed into water and concentrated to 90 per cent phosphoric acid by evaporation and distillation. This process permits the recovery of 98-99 per cent of the phosphorous pentoxide content of the phosphate rock in contrast with the 94-95 per cent recovery possible by normal wet process methods using sulphuric acid.

A semi-commercial plant with a daily production of one ton of phosphoric pentoxide (as 80 per cent phosphoric acid) is being operated at Haifa. Another plant with a capacity of 7 tons of phosphoric acid a day has been constructed for Toyo Soda Manufacturing Co. in Japan. The

acid is sold in three grades viz. 89, 85 and 75 per cent phosphoric acid.

[Chem. Trade J. & Chem. Engr., 154 (1964), 4,007, 435].

### Potassium Fertilizers from Sea Water

Potassium is an essential plant nutrient, and potassium compounds like chloride, sulphate, nitrate and phosphate are used widely for improving the size and weight of roots, seeds and fruits, strength of the cereal plants and generally for rapid growth of crops like sugarcane, potato, tomato, sugarbeet, paddy, barley, cotton and some of the fruit crop. In countries practising agricultur<sup>e</sup> scientifically, the application of nitrogen and potassium fertilizers is in the ratio  $N : K_2O :: 1 : 1.5$ .

In India there are no natural potash deposits except that about 15,000 tons of potassium nitrate are being obtained every year from surface soil in the U.P., Bihar, Madras, Punjab and Orissa. There are of course a large number of potassium-bearing rocks with varying potassium contents, and there is possibility of recovering potassium sulphate from feldspar. The process consists of sintering the raw mix containing feldspar, limestone and gypsum at 900–1,050°C. The sintered material is leached for recovery of potassium sulphate, and the sludge is then burnt to obtain white cement clinker. White cement factories can be established in Rajasthan, Madras and Andhra Pradesh, based on the availability of potassium bearing raw materials and other factors in which potassium sulphate will be obtained as a byproduct.

The other source of potassium salts is the bittern left over after crystallization of common salt from sea-water (at 29°Be), containing about 2–2.5 per cent of potassium chloride. The bittern is further evaporated to crystallize out a mixed salt containing mainly potassium chloride, magnesium sulphate, magnesium chloride and sodium chloride. Where it is difficult to attain higher densities due to the prevailing humidity conditions, it is advantageous to add magnesium chloride or a concentrated bittern of 36°Be to this bittern for obtaining separation of mixed salt at lower densities. For every 1,000 tons of salt, about 80 tons of mixed salt, containing about 15–20 per cent of potassium chloride, are obtained.

In a paper presented at the ECAFE Conference on the Development of Fertilizer Industry in Asia and the Far

East, held in Bombay during November 18 to December 2, 1963, Dr. D. S. Datar of the Central Salt and Marine Chemicals Research Institute, Bhavnagar, has described some of the processes for the recovery of fertilizer grade (-) potassium chloride and potassium sulphate from mixed salt developed in his laboratory.

In one process, the crushed mixed salt is extracted at 110°C with a dissolving brine containing sodium chloride and magnesium chloride. The potassium chloride and magnesium sulphate go into solution while the sodium chloride and other impurities from mixed salt remain undissolved. On cooling the hot filtrate to 20°C potassium and sodium chlorides separate while magnesium sulphate remains in solution. The mother liquor is utilized for recovery of epsom salt by cooling it to 15°C and the mixture of potassium chloride and sodium chloride is saturated with a saturated solution sodium chloride at 100°C in which potassium chloride goes into solution. The filtrate on cooling to 20°C deposits potassium chloride. The Institute has set up a semi-commercial plant at Kandla to manufacture 3 tons of potassium chloride and 10 tons of epsom salt per day.

By another process, involving extraction of the mixed salt by hot concentrated bittern (36°Be), carnallite is separated, which is decomposed by water treatment. The potassium chloride obtained is recrystallized. The State Trading Corporation of India is setting up a semi-commercial unit based on this process at Tuticorin.

In another process the mixed salt solution is treated with theoretically required quantity of soda ash solution to precipitate magnesium as magnesium carbonate trihydrate, which is filtered. The filtrate after concentration is cooled to 0°C when Glauber's salt is separated, and the filtrate from this is taken for fractional crystallization at 100°C. Sodium chloride is crystallized first and then by cooling the residual filtrate to room temperature potassium chloride is crystallized out.

Two types of conditioners viz., inorganic inert powders and hydrophobic organic compounds have been developed for preventing caking of potassium chloride.

Processes for the recovery of potassium sulphate from the mixed salt as potassium schonite, syngenite and potassium sul-

phate have also been developed at this Institute.

Potassium schonite, which is a double sulphate of potassium and magnesium, with six molecules of water, is obtained by flotation of mixed salt using octadecylamine acetate and highly sulphonated castor oil.

Syngenite, which is a double sulphate of potassium and calcium with one molecule of water, is obtained by grinding mixed salt and marine gypsum together and the mixture left overnight with added water to complete the reaction. About 70 per cent of potassium is obtained as syngenite, while the mother liquor is recycled to recover the potassium left over.

Potassium sulphate is also obtained from potassium schonite by treatment with excess potassium chloride. A process for direct recovery of potassium sulphate from mixed salt and another for the manufacture of potassium metaphosphate from potassium chloride and phosphoric acid for Indian conditions are being worked out at the CSMCRI. The author has discussed various points such as capital investment required for setting up commercial units for the manufacture of potassium chloride. Salt works producing 100,000 tons of common salt will yield about 8,000 tons of mixed salt from which about 1,000 tons of potassium chloride can be recovered. The economical size of potassium chloride plant is 3 tons per day or about 1,000 tons per year, and therefore the salt factories producing 100,000 tons or more can commercially exploit one of the above three processes, while smaller salt works can combine to work them out. The present common salt production in India is over 3.8 million tons, and from these salt works about 30,000 tons of potassium chloride can be made available out of which 8,000 tons can be produced in the five major salt works in Gujarat using the mixed salt as the starting material.

### Cost of Synthetic Ammonia

The two main factors controlling the economy of ammonia production are the feedstock used for synthesis gas manufacture and the cost of utilities, particularly power. The raw materials used are either of the following: coal/lignite, coke, natural gas, coke oven gas, refinery gas, fuel oil/naphtha and hydrogen from electrolysis of water. In a paper, entitled

'Analysis of Possible Investment and Production Costs for Alternative Schemes for Production of Ammonia', presented at the ECAFE Conference on the Development of Fertilizer Industry, held at Bombay during November 18 to December 2, 1963, Mr. K. S. Vishwanathan and Dr. S. K. Mukherjee have evaluated the relative costs for alternative feedstocks for the manufacture of ammonia synthesis gas from the following: I. coke in slagging gas generator, II. coal by its direct gasification at atmospheric pressure in powdered state, III. coke oven gas by separating hydrogen by low temperature fractionation and either (a) utilising it alone in ammonia production or (b) by utilising both the hydrogen and the hydrocarbon streams by reforming the latter, with steam and oxygen, and IV. fuel oil/naphtha by non-catalytic partial oxidation under pressure. The projected alternatives assume a common basis of production of 230 metric tons of ammonia per day and 345 stream days per year.

In all the alternatives considered by the authors, high pressure desulphurisation was based on Giammarco-Vetrocoke process and in the case of III(b) the raw coke oven gas is purified in conventional purifier boxes followed by Vetrocoke process. The carbon monoxide conversion unit forms an essential step, except in III(a). Pressure conversion of carbon monoxide was adopted in all the cases, and for carbon dioxide removal the process based on alkali scrubbing and for carbon monoxide removal liquid nitrogen wash were considered. The end pressure for synthesis as 350-400 atmospheres was assumed for all alternatives.

The Kcal requirement in the form of raw materials and electric power on totalling indicate that the alternatives III(a) and III(b) have the highest process efficiency (Table I).

TABLE I—RAW MATERIAL & POWER REQUIREMENTS IN DIFFERENT SYNTHESIS GAS PROCESSES

Alternative	Raw Material & Electric Power Requirement Expressed as Kcal $\times 10^6$	Relative Index
I	10.55	136
II	11.83	152
III(a)	7.77	100
III(b)	7.83	101
IV	8.06	104

The plant investment cost comprises the following: costs for machinery, freight, insurance, customs, port and inland handling, civil engineering construction and erection of plant; cost of coke oven plant and other auxiliaries if necessary; and working capital cost. In calculating the production costs, the incidence of capital charges were computed as: depreciation 10 per cent of the plant cost, maintenance material 3 per cent, services 2 per cent and interest on capital 6 per cent of the capital outlay. For maintenance labour costs and for overheads 100 per cent of the direct operational labour costs were assumed. The relative index for investment for the alternatives was as below:

Alternative	Relative Index for Erected Plant Cost	
	(i)	(ii)
I	118	122
II	118	167
III(a)	293	100
III(b)	149	113
IV	100	139

(i) includes coke oven and byproduct plant for alternatives I and III; (ii) excludes coke ovens and byproduct plants for alternatives I and II.

The investment requirement for the alternative III(a) according to the authors is the highest, followed by alternative III(b) if the investment requirement for coke ovens and byproduct plants is also taken into account. The alternative III(a) could be considered only near a steel-works where surplus coke oven gas and nitrogen are available, and in this case the ammonia would be the cheapest provided coke oven gas and the utilities are available at reasonable technologically correct prices. The investment in alternative II for the gas and ammonia is the highest, and the production cost of ammonia would be high.

In the alternative III(b) the investment required is the least for gas and ammonia plants in comparison with alternatives I, II and IV.

A comparative study of the alternatives I and IV indicated that process efficiency of IV is better while the production cost is about the same. The investment for IV is also less.

#### Price of Urea

Govt. of India have decided to reduce the pool issue price of urea

from Rs. 670.00 per metric ton to Rs. 570.00. This reduction is aimed at preparing the ground for intensive utilisation of urea and popularising it among the cultivators, as a prelude to its large-scale manufacture in the country.

[FCI News, 2 (1964) 3, 16]

#### Production at Nangal

The production figures of fertilizer (calcium ammonium nitrate) and heavy water at the Nangal Unit of the Fertilizer Corporation of India have well exceeded the schedule for the third year in succession. The final production figure of fertilizer for 1963-64 is 3,74,000 tons as against the target of 3,70,000 tons, and for heavy water 11,733.4 Kg. as against the target of 11,500 Kg. The factory switched over to full-scale production only since November 16, 1962, while the heavy water plant was commissioned only on August 9, 1962. The despatches of this fertilizer to different parts of the country from Nangal are also a record.

The performance of this Unit in past years was also exemplary. During 1961-62, the first full year of the working, the factory produced 2,00,790 tons of fertilizers against the target of 2,00,000 tons and during 1962-63, 2,84,322 against the target of 2,80,000. In the case of heavy water, its production during 1962-63 was 5,250 Kg. against the target of 4,000 Kg.

[FCI News, 2 (1964), 4, 2]

#### Gujarat State Fertilizers Co.

The Gujarat State Fertilizers Co. Ltd. is setting up a complex fertilizer factory near Baroda for manufacturing 150,000 tons of ammonia and 100,000 tons of urea per annum, and is establishing plants with daily capacities of 470 tons of sulphuric acid, 165 tons of phosphoric acid, 470 tons of ammonium sulphate from by-products gypsum and 341 tons of diammonium phosphate 18 : 46 grade. Ammonium sulphate and diammonium phosphate will be granulated to yield 356,000 tons of ammonium phosphate sulphate (AMOPHOS) of 19.5 : 19.5 grade. The project will also produce 3,200 tons of technical grade urea. The following are the processes to be used: (i) Gas synthesis for hydrogen and nitrogen by the ICI Steam Naphtha Reforming Process, using natural gas, associated gas and naphtha hydrocarbons in any combination to be engineered by Power Gas Corporation of U.K.; (ii) high pressure Casale process for

ammonia synthesis; (iii) Toyo-Koatsu total recycle process with latest innovations for urea synthesis (Japanese process); (iv) Toyo-Koatsu process for technical grade urea; (v) Titlestad process (USA) for sulphuric acid; (vi) Dorco process for phosphoric acid; (vii) Chemico (U.S.A.) process for ammonium sulphate and ammonium phosphate.

The investment cost per ton of ammonia will be about Rs. 500.00 and of urea about Rs. 260.00. This Company is expected to enter the capital market very soon with a total equity issue of about Rs. 15 crores. The Government of Gujarat is expected to take up 47-48 per cent of the shares, and a number of leading industrialists, who have joined the Board of Directors, are likely to take up shares of a total of about Rs. 2 crores.

[Fertilizer News, 9 (1964), 4, 31]

### Self-sufficiency in Nitro Fertilizers

According to a study prepared by the Union Ministry of Petroleum & Chemicals, a tentative production target of 1.75 million tons of nitrogen has been fixed for the Fourth Plan. At this stage it is not possible to indicate when the country would be able to achieve self-sufficiency, and in future the demand is expected to rise because of the increasing popularity of chemical fertilizers. Against the Plan target of 800,000 tons of nitrogen by the end of Third Plan, the production according to the present estimate will not be more than 4 to 4.5 lakh tons. The progress is however expected to be greatly accelerated during the first two years of the Fourth Plan, when several of the new units are likely to go into full production.

As regards the manufacture of phosphate fertilizers, the stage of self-sufficiency has already been reached.

[Chem. Weekly, 8 (1964), 52, 4]

### Fertilizer Research Company

Ten British fertilizer manufacturers have together set up a new research and development company, Fertilizer Development Ltd., to concentrate on the manufacture of granular compounds. The new organization, which will deal with every aspect of compound manufacture—suitability of raw material for formulation, plant design, control of granulation conditions, mechanical handling, packaging, etc.—will aim at narrowing the gap between available know-how and its effective

utilization. It will resemble the information and development department of a research association with the practical work being carried out at the premises of the 10 founder firms.

[Chem. Age, 91 (1964), 2331, 406]

### Liquid Sulphur Dioxide as Fertilizer

As a result of experiments at Washington State University by S. Roberts and F. E. Koehler, it has been found that liquid sulphur dioxide can be injected directly into the soil to serve as a source of nutrient sulphur for plants. In both green house and field trials, response of wheat grown on sulphur-deficient silt loam to sulphur dioxide compared favourably with that from calcium sulphate.

In green house trials, sulphur dioxide applied at a rate of 2.5 ppm sulphur approximately doubled wheat yields. Plant growth and responses to sulphur dioxide at rates 2.5 to 500 ppm sulphur, and gypsum at 10 ppm were almost identical. At rates of 2,500 ppm sulphur, sulphur dioxide reduced greatly plant growth.

In field trials, sulphur dioxide was applied at rates of 8, 16, 32 and 64 lb sulphur per acre, and no adverse effect was noted even at the highest rates of application.

[Chem. Tr. J. & Chem. Engr., 154 (1964), 4,005, 362]

### Fertilizer Plant at Durgapur

Prof. H. Kabir, Union Minister of Petroleum & Chemicals, stated in the Lok Sabha that the Fertilizer Corporation of India Ltd. after a preliminary review had, on the whole, favoured the setting up of the proposed fertilizer plant at Durgapur. However, before a final decision was taken, the Government would have to await recommendations made by the Technical Committee.

[Chem. Weekly, 8 (1964), 49, 5]

### Conference, Symposium, Etc.

1. *Testing and Evaluation of Materials:* To commemorate its Golden Jubilee, the Government Test House at Alipore, Calcutta, organised a symposium on Testing and Evaluation of Materials during March 21 to 23, 1964, covering the following aspects: importance of testing and evaluation of materials in the context

of economic development of the country, statistical and mathematical approach to testing, non-destructive testing of materials, testing and standardization of electrical engineering materials and appliances, recent advances in the testing and evaluation of boilers and pressure vessels, testing and evaluation of metals including finished engineering materials, chemical products consisting of petroleum products and lubricants, ores, minerals, ceramics, paper and paper products, rubber and plastics, leather, paint and pigments, modern physico-chemical methods of testing and analysis, materials for building and road construction and sanitary fittings, textile and allied materials, and precision engineering measurements.

Drs. B. K. Banerjee, Dy. Superintendent, and H. C. Roy, Technologist, and Sarbasri A. K. Chakravarty and G. S. Sinha, both Assistant Technologists, of the Planning & Development Division, attended the symposium as official delegates. Dr. Banerjee presented a paper entitled "Modern Physico-chemical Methods of Testing Fertilizer Materials with Particular Reference to their Utility in Industry." The paper dwelt on the application of Electron Microscopy, Differential Thermal Analysis, X-ray, Spectroscopy, etc. in the qualitative control of the finished products and raw materials in the fertilizer industry.

2. *Salt and By-Products:* A seminar on Salt and By-Products was held at the Central Salt & Marine Chemicals Research Institute, Bhavnagar during April 10 and 11, 1964, which was attended by Sarbasri J. M. Sarkar, Assistant Superintendent, Asutosh Mukherjee, Assistant Technologist, S. Ranganathan, Research Chemist, and D. K. Malhotra, Research Engineer, as delegates from this Division. Among the papers presented several were on the economic recovery of by-products of salt with special reference to potash, of which the following may be mentioned (i) 'Recovery of Potash from Sea' by R. P. Daroga, (ii) Flotation of Potassium Salts' by N. N. Udwadia and G. T. Gadre, (iii) 'Recovery of By-products from Brine and Bitterns at the Government Model Salt Farm at Wadala, Bombay' by B. Revanna. Our delegates had fruitful discussions with the staff of CSMCRI on the recovery of potash in view of its rapidly growing consumption. They also visited the Model Salt Farm at Wadala and had useful discussions with Sri Revanna.

# STATISTICS

TABLE 1—TARGETS OF CONSUMPTION OF NITROGENOUS, PHOSPHATIC AND POTASSIC FERTILIZERS IN INDIA

('000 tons)

Year	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
1960-61	230	70	25
1961-62	400	100	82
1962-63	525	150	100
1963-64	650	225	130
1964-65	800	300	160
1965-66	1,000	400	200

[Third 5 Yr. Plan, Planning Commission, Govt. of India, Manager of Publications, Delhi (1961)]

TABLE 2—TARGETS OF PRODUCTION OF NITROGENOUS AND PHOSPHATIC FERTILIZERS IN INDIA

('000 tons)

	N	P <sub>2</sub> O <sub>5</sub>
1961-62	140	100
1962-63	200	150
1963-64	300	225
1964-65	500	300
1965-66	800	400

[Fertilizer Statistics 1962-63, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 3—END-PRODUCTS PATTERN OF NITROGENOUS AND COMPLEX FERTILIZERS IN INDIA (1965-66)

('000 tons of N)

Ammonium Sulphate	230
Ammonium Sulphate Nitrate	30
Nitro-chalk and nitro-limestone	160
Nitro-phosphate and complex fertilizers	45
Urea	305
Ammonium Phosphate	200
Ammonium Chloride	30
Total	1000

[Fertilizer Statistics 1962-63, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 4—OVERALL INVESTMENT IN FERTILIZER FACTORIES IN INDIA

(Rupees) in crores

Overall investment on capital account	225
Foreign exchange cost	100

[Fertilizer Statistics, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 5—STATEWISE TARGETS OF CONSUMPTION OF FERTILIZERS

('000 tons)

State/ Union territory	Ammonium Sulphate		Superphosphate		Potassium chloride	
	1960-61	1965-66	1960-61	1965-66	1960-61	1965-66
Andhra Pradesh	273	524	90	350	—	—
Assam	10	60	5	25	—	—
Bihar	50	400	15	120	1	20
Gujarat	95	300	48	90	—	13
Maharashtra	100	581	53	324	—	—
Kerala	37	191	7	190	1	56
M. P.	26	200	5	40	—	—
Madras	150	580	60	320	12	90
Mysore	87	300	20	320	—	11
Orissa	30	200	8	50	—	2
Punjab	40	280	2	24	—	—
Rajasthan	15	100	4	33	—	—
U. P.	297	990	60	300	8	80
West Bengal	40	500	25	250	—	—
Jammu & Kashmir	4	14	—	—	—	—
Delhi	1	1	—	—	—	—
Himachal Pradesh	—	1	—	1	—	—
Pondicherry	25	25	2	5	1	6
Total	1,280	5,247	404	2,442	23	278*

\*In terms of K<sub>2</sub>O the consumption target should be 200,000 tons. The lower figure as compared to that given in Table 1 is due to the fact that it does not take into account the consumption figures of other States for which information is not available.

[Third 5 Yr. Plan, Planning Commission, Govt. of India Manager of Publications, Delhi (1961)]

TABLE 6—PRICES OF FERTILIZERS PER METRIC TON

(Pool Fertilizers)

Date	Price in Rs. when Sold for the Use of Plantations				Price in Rs. when Sold for the Use of Cultivators				Remarks
	In W. Bengal, Assam, Manipur & Tripura	In any other State or Union Territory	In U.P.	In Madras	In Orissa	In any other State or Union Territories			
Ammonium Sulphate									
1.1.1962	..	..	401.30	384.60	366.00	370.20	370.00	360.00	Exclusive of sales tax and other local taxes, wherever levied except in the case of Madras where the price is inclusive of sales tax and other local taxes.
5.10.1962	..	..	384.60	384.60	366.00	370.20	370.00	360.00	
Ammonium Sulphate Nitrate									
1.1.1962	..	..	451.50	435.00	438.00	442.30	435.00	435.00	,, ,,
5.10.1962	..	..	435.00	435.00	438.00	442.30	435.00	435.00	

[Fertilizer Statistics, 1962-63, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 7—PRICES OF FERTILIZERS

(Non-Pool Fertilizers)

Fertilizers			Period	Price Rs. per metric ton	Remarks
Ammonium Chloride	..	..	Jan. 1962	452.00*	Factory price f.o.r. destination
Chilean Natural Sodium Nitrate	..	..	May 1963	283.00	Retail price fixed by Govt. for sale to cultivators.
Ammonium Phosphate Sulphate (N 16%, P <sub>2</sub> O <sub>5</sub> 20%)			—	525.00	Ex-factory, sales tax extra
Ammonium Phosphate Sulphate (N 20%, P <sub>2</sub> O <sub>5</sub> 20%)			Aug. 1963	565.00	Pool price of imported material
Nitrophosphate (N 12.9% P <sub>2</sub> O <sub>5</sub> , 12.9%)	..	..	Aug. 1963	375.00	Pool price of imported material
Superphosphate (P <sub>2</sub> O <sub>5</sub> 16%)	..	..	June 27, 1962	193.50	These ex-works prices apply only to factories situated within 100 miles of sea ports for materials packed in alkathene lined jute bags 100 kilo capacity. Those situated further inland would charge an extra premium to cover transport costs of raw materials. When supplies are required in 50 kilo packings, the manufacturers may charge extra at the rate of Rs. 5.00 per metric tonne.
Superphosphate (P <sub>2</sub> O <sub>5</sub> 18%)	..	..	Aug. 1963	207.50	
Potassium Chloride (K <sub>2</sub> O 60%)	..	..	April 1963	285.28	Ex-godown at port
				273.46	Ex-jetty
Potassium Chloride (K <sub>2</sub> O 50%)	..	..	Sept. 1963	230.73	Ex-godown at port
				220.88	Ex-jetty

\* Includes Rs. 38.40 being the commission and distribution charges permitted by U.P. Govt.

[Fertilizer Statistics 1962-63, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 8—SUBSIDY ON FERTILIZERS

<i>Fertilizers/State</i>	<i>Subsidy</i>
<b>SUPERPHOSPHATE</b>	
Andhra Pradesh ..	—
Assam ..	25% on the cost price including transportation and other incidental charges.
Bihar ..	20% on the sale price
Gujarat ..	—
Jammu & Kashmir ..	—
Kerala ..	12.5% on the value
Madhya Pradesh ..	25% on the sale price
Madras ..	—
Maharashtra ..	Rs. 20 per ton <sup>1</sup>
Mysore ..	—
Orissa ..	m
Punjab ..	25% on the sale price
Rajasthan ..	25% on the sale price
Uttar Pradesh ..	25% on the retail sale price in 15 backward districts in the eastern region
West Bengal ..	25% on the sale price
Delhi ..	25% on the sale price
Himachal Pradesh ..	25% on the cost, 50% on the remaining cost on transportation
Andamans ..	50% on the sale price
Manipur ..	n
Pondicherry ..	25% on the sale price
Tripura ..	50% on the sale price
<b>NITROPHOSPHATE</b>	
Maharashtra ..	Rs. 20.00 per ton <sup>1</sup>
<b>MIXED FERTILIZERS</b>	
Maharashtra ..	Rs. 20.00 per metric tonne on the purchase of approved grades of fertilizer mixtures. <sup>2</sup>

m: A proposal for allowing a subsidy of Rs. 15.00 per tonne is under consideration.

n: No financial provision for the subsidy is required.

<sup>1</sup>: Given to the cultivators, excluding those in concentrated sugarcane areas.

<sup>2</sup>: Effective during April 1963 to February, 1964

[Fertilizer Statistics 1962-63, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 9—OFF-SEASON REBATES FOR NITROGENOUS FERTILIZERS (Rs. per metric ton)

The off-season rebate is admissible on the following nitrogenous fertilizers supplied by the Central Pool: ammonium sulphate, urea and calcium ammonium nitrate. The rebate is admissible at the following graduated rates on despatches made by the Pool during the different months of the non-manuring quarter.

<i>Fertilizer</i>	<i>1st Month</i>	<i>2nd Month</i>	<i>3rd Month</i>
Ammonium Sulphate and Calcium Ammonium Nitrate	7.50	5.00	2.50
Urea .. ..	12.00	8.00	4.00

[Fertilizer Statistics 1962-63, Fertilizer Assn. of India, New Delhi (Nov. 1963)]

TABLE 10—WORLD PRODUCTION &amp; CONSUMPTION OF NITROGEN

(thousand tonnes of nitrogen)

## Summary of the Different Regions

		1962-63		1963-64	
		<i>Production</i>	<i>Consumption</i>	<i>Production</i>	<i>Consumption</i>
W. Europe ..	5,581	4,523	5,865	4,640	
E. Europe ..	2,424	2,358	2,688	2,575	
Africa ..	250	461	261	501	
N. America ..	4,623	4,560	4,820	4,820	
C. America ..	116	347	225	372	
S. America ..	222	213	268	267	
Asia ..	2,191	3,064	2,392	3,246	
Australia ..	27	60	35	70	
World Total ..	15,434	15,586	16,554	16,491	

## Country-wise Breakdown

		1962-63		1963-64	
		<i>Production</i>	<i>Consumption</i>	<i>Production</i>	<i>Consumption</i>
<i>Western Europe</i>					
Austria ..	185	66	195	69	
Belgium ..	300	130	300	130	
Cyprus ..	—	12	—	14	
Denmark ..	—	147	10	144	
Eire ..	—	35	—	37	
Finland ..	44	66	55	69	
France ..	916	815	930	860	
W. Germany ..	1,467	1,005	1,530	1,010	
Greece ..	—	90	5	99	
Iceland ..	8	10	8	10	
Italy ..	820	471	860	485	
Netherlands ..	482	316	490	315	
Norway ..	322	61	350	61	
Portugal ..	83	80	87	85	
Spain ..	156	345	220	360	
Sweden ..	63	130	70	138	
Switzerland ..	35	28	35	29	
Turkey ..	20	28	25	30	
U. K. ..	680	688	695	700	
Total W. Europe	5,581	4,523	5,865	4,640	

	1962-63		1963-64	
	Production	Consumption	Production	Consumption
<i>Eastern Europe</i>				
Bulgaria ..	108	125	130	138
Czechoslovakia ..	161	195	185	205
E. Germany ..	397	290	410	290
Hungary ..	75	110	80	117
Rumania ..	40	38	40	45
Poland ..	315	310	330	320
U.S.S.R. ..	1,303	1,170	1,463	1,330
Yugoslavia ..	25	120	50	130
Total E. Europe	2,424	2,358	2,688	2,575
<i>Africa</i>				
Algeria ..	—	15	—	18
Egypt ..	135	225	141	236
Mauritius ..	—	10	—	12
Morocco ..	—	12	—	14
Nigeria ..	—	2	—	3
Reunion ..	—	5	—	7
Rhodesia ..	—	38	—	41
S. Africa ..	115	110	120	115
Sudan ..	—	25	—	25
Tunisia ..	—	4	—	5
Others ..	—	15	—	25
Total Africa ..	250	461	261	501
<i>North America</i>				
Canada ..	471	140	490	150
U.S.A. ..	4,152	4,420	4,330	4,670
Total N. America	4,623	4,560	4,820	4,820
<i>Central America</i>				
British West Indies	26	25	95	30
Costa Rica ..	—	10	—	10
Cuba ..	25	70	30	70
Dominican Rep.	—	9	—	9
El Salvador	—	13	—	17
Guadeloupe and Martinique	—	8	—	8
Guatemala ..	—	9	—	9
Honduras ..	—	10	—	15
Mexico ..	65	175	100	183
Others ..	—	18	—	21
Total Central America	116	347	225	372

	1962-63		1963-64	
	Production	Consumption	Production	Consumption
<i>South America</i>				
Argentina ..	5	12	5	15
Brazil ..	22	75	25	85
British Guiana	—	5	—	6
Chile ..	170	26	190	26
Colombia ..	10	40	25	55
Ecuador ..	—	6	—	7
Peru ..	15	35	15	50
Uruguay ..	—	5	—	7
Venezuela ..	—	8	8	15
Others ..	—	1	—	1
Total S. America	222	213	268	267
<i>Asia</i>				
Ceylon ..	—	35	—	35
China ..	400	760	450	800
Indonesia ..	—	110	15	120
India ..	212	460	261	481
Iran ..	—	12	2	20
Iraq ..	—	2	—	2
Israel ..	26	28	26	28
Japan ..	1,291	819	1,320	830
Jordan ..	—	1	—	1
Lebanon ..	—	10	—	11
Malaya/Singapore	—	32	—	32
N. Korea ..	90	100	90	100
S. Korea ..	40	185	56	210
Philippines ..	22	65	22	65
Ryukyu ..	—	8	—	18
Syria ..	—	15	—	15
Taiwan ..	70	135	75	150
Thailand ..	—	12	—	13
Vietnam ..	—	35	—	45
Pakistan ..	40	90	75	110
Others ..	—	150	—	160
Total Asia ..	2,191	3,064	2,392	3,246
<i>Australasia</i>				
Australia ..	27	50	35	59
New Zealand	—	8	—	9
Fiji ..	—	2	—	2
Total Australasia	27	60	35	70

[From Brit. Sulphur Corpr's Annual Statistics, Nitrogen (1964), 27, 12-13]

TABLE 11—DOMESTIC PRICES OF FERTILIZERS

## United Kingdom

<i>Sterling per ton delivered to farm (early delivery rebate)</i>						
	Nov./Dec. 1963		Subsidy		E. D. R.	
	£	s. d.	£	s. d.	£	s. d.
Sodium nitrate (16%N)	22	3 0	5 14 8		1 0 0*	
Ammonium Sulphate (21%N)	19	8 6	7 10 6		10 6**	
Nitro-chalk (21%N)	21	10 0	7 10 6			
Kay-nitro (16:0:16)	24	5 0	5 14 8			
Nitra-Shell (23%N)	23	11 0	8 4 10		1 8 0†	

\*November for delivery by 29 February. \*\* 7s. for December for despatch by 31 January. †Combined E.D.R./Storage.

## United States

Ammonia, anhydrous	
Fertilizer grade	\$ 92 per s. ton tank cars ex-works
Refrigeration grade	\$ 94.50 per s. ton tank cars ex-works
Ammonium Sulphate (20.5%N)	
Standard	\$ 30 s. ton bulk f. o.b. plant
Granular	\$ 35 s. ton bulk f.o.b. plant
Nitrogen solutions	
Direct application	\$ 1.64 per unit s. ton tank cars ex-works
Manufacturing	\$ 1.32 per unit s. ton tank cars ex-works

## Urea

Fertilizer grade (45%N)	\$ 86 s. ton bulk delivered
Fertilizer grade (46%N)	\$ 88 s. ton bulk delivered
Industrial grade (46%N)	\$ 100 s. ton in bags delivered
Calcium ammonium nitrate (20.5% N)	\$ 48 s. ton bags f.o.b. cars at plant
Ammonium nitrate (33.5%N)	\$ 67 per s. ton in bags f.o.b plant

## France

*N.Fr. per 100kg. delivered in bulk in 20 tonne lots railway*

	November 1963		December 1963	
	without taxes	with taxes	without taxes	with taxes
Ammonium sulphate				
21%N ..	25.62	28.47	26.39	29.32
Urea (Perlurea) 46%N	47.40	52.67	48.60	54.00
Lime Ammonium Nitrate (Ammonitrate)				
20.5%N ..	22.94	25.49	23.63	26.26
27.5%N ..	28.73	31.92	29.60	32.89
33.5%N ..	34.16	37.96	35.02	38.91
Calcium nitrate				
15%N ..	22.20	24.67	22.87	25.41
15.5%N ..	22.94	25.49	23.63	26.26
Calcium magnesium nitrate 13%N ..	21.01	23.34	21.65	24.06
Ammonium nitrate				
33.5%N ..	33.17	36.86	34.00	37.78
34.5%N ..	34.16	37.96	35.02	38.91
Sodium nitrate 16%N	26.94	29.93	27.30	30.33

[Nitrogen (1963), 26, 13]

# TECHNOLOGY

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The opinions expressed by the authors are their own and do not necessarily reflect the views of the Planning and Development Division of the Fertilizer Corporation of India Ltd.



# X-Ray Study of Ammonium Nitrate Sulphate Fertilizer

By

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Evidence of the presence of varying molecular composition of ammonium nitrate sulphate, double salts having 1 : 1, 2 : 1 and 3 : 1 molar ratio of ammonium nitrate: ammonium sulphate, has been found by the x-ray diffraction analysis. Amongst these the existence of the second and third species was reported earlier in the literature. The commercial double salt—manufactured at Sindri—was also included in the present investigation. So far no evidence of any intermediate species between the aforesaid molecular compositions of double salt has been found from the physical and chemical data.

## Introduction

In the field of fertilizer technology, the nature and characterisation of the raw materials and end-products are important. Various complexities, such as the methods of their preparation, the nature of their impurities, caking characteristics, etc. have led to the study of their physical properties including their crystal forms, their phase transitions, etc. All the information has been utilized rightly for the production of better grade fertilizers. Numerous investigations to this end have already been reported, viz. on ammonium nitrate which is hygroscopic and prone to explosive hazard.<sup>1-6</sup> On the other hand, ammonium nitrate sulphate, a double salt, was found to be less hygroscopic in nature and far less dangerous to handle. Therefore, attempts are being made by several workers to prepare different types of this compound, comprising various types of molecular ratio of ammonium nitrate and ammonium sulphate.<sup>1-6</sup> Already some industrial concerns have taken up the production of this double salt<sup>7</sup>. Some interesting observations on the following compositions, viz. 2:1 and 3:1 of  $\text{NH}_4\text{NO}_3$ :  $(\text{NH}_4)_2\text{SO}_4$ , are already available in the literature<sup>1-6</sup>.

Preliminary powder x-ray and optical data for the 2:1 and 3:1 double salts were reported by Sokolov<sup>1</sup>. Optical data and unit cell constants for 2:1 salt were reported by Janecke, Eissner and Brill<sup>2</sup>. Bragg also reported the unit cell constants for 2:1 salt considering the symmetry as triclinic<sup>3</sup>. Recently, Smith, Lehr and Frazier have reported the morphological, optical, x-ray diffraction and unit cell parameters of the ammonium nitrate sulphate, viz.  $3\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $2\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ <sup>4</sup>. According to them, both belong to

the monoclinic system, and there are no intermediate species between the two varieties. It is to be noted, however, that none of the above authors are in agreement with one another. Therefore, the present investigation comprises the re-examination of the earlier reports on the x-ray data for 2:1 and 3:1 salts, as well as the exploration of the possibilities of formation of the different types of double salts under various physical conditions. In this investigation, the double salt manufactured at Sindri has also been included. The object of this work is to elucidate their crystal-phase composition and the state of aggregation.

## Experimental

In the laboratory, the crystals of the double salts were prepared by the following methods: 1(a) Saturated ammonium sulphate solution was mixed with the saturated solution of ammonium nitrate in the different mole ratios and left for crystallisation at room temperature; (b) the procedure was similar to the above, except that the solution compositions were being made strongly basic with ammonium hydroxide. 2. The solution compositions in the different mole ratios were heated at 60°-70°C and then cooled slowly.

It may be worth recounting here briefly the process of manufacture of double salt followed by the Sindri Unit of F.C.I. Ltd. which is as follows: Concentrated ammonium nitrate solution is sprayed on the crystals of ammonium sulphate, and both the materials are mixed in a rotary drum and then crystallised. The technical grade nitrate-sulphate of ammonia of normal composition contains 38 per cent of ammonium nitrate and 62 per cent of ammonium sulphate by weight. The chemical

characterisation of the precipitated crop and the commercial double salts is given in Table 1.

X-ray diffraction patterns of the above samples were obtained in RKD\* camera (Cassette diameter 57.3 mm.) with CuK $\alpha$  radiation using nickel filter at 30 KV, 20 mA giving 6 hr exposure to each sample (Fig. 1). The interplanar distances of the lattices were calculated from the measurement on x-ray diffraction patterns with maximum accuracy. The intensities of lines on the x-ray diffraction pattern were evaluated by visual estimation. The x-ray powder data are given in Tables 2A & 2B. Optical data and x-ray data on 3:1 and 2:1 salts obtained by previous authors are given in Table 3.

\* Russian equipment

Fig. 1. X-ray Photographs.  
Radius of Camera 5.73 cm.  
Radiation Cu K $\alpha$  1.54 Å  
Time of Exposure 6 hr.

- 1. Ammonium Nitrate
- 2. Ammonium Suhphate
- 3, 4 & 5 Double Salts 1:1, 2:1 & 3.1 (Alkaline media).
- 6. Double Salt (Sindri).

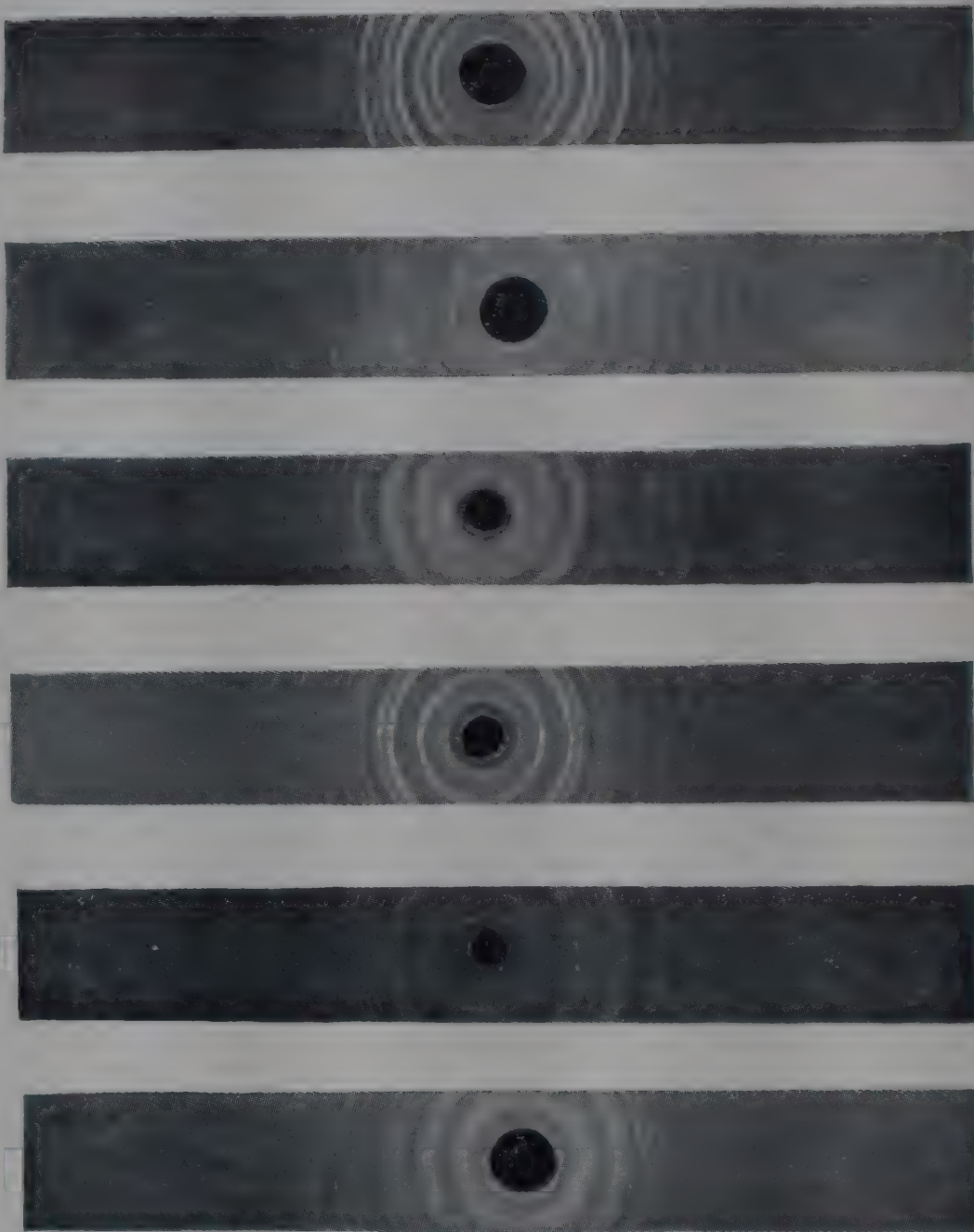


TABLE 1—CHEMICAL CHARACTERISATION OF THE DOUBLE SALTS

Salts	Chemical Analysis, %						Empirical Composition
	<div><div><div><math>NH_4</math></div><div><math>NO_3</math></div><div><math>SO_4</math></div></div></div>						
Commercial No. 1 .. ..	23.14	32.93	43.93	Approximately $2NH_4NO_3 \cdot 3(NH_4)_2SO_4$			
(Sindri) No. 2 .. ..	22.89	24.33	52.77				
Theoretical .. ..	25.89	22.30	51.98				
Laboratory 4 : 1							
$NH_4OH$ media .. ..	25.24	29.19	45.43	$NH_4NO_3 \cdot (NH_4)_2SO_4$			
Theoretical .. ..	25.48	29.25	45.29				
Laboratory 6 : 1							
$NH_4OH$ media .. ..	25.00	41.50	33.50	$2NH_4NO_3 \cdot (NH_4)_2SO_4$			
Theoretical .. ..	24.65	42.46	32.46				
Laboratory 8 : 1							
$NH_4OH$ media .. ..	25.70	49.20	25.10	$3NH_4NO_3 \cdot (NH_4)_2SO_4$			
Theoretical .. ..	24.24	50.06	25.66				

## Discussions

The x-ray photograph of each specimen was analysed with particular reference to the crystal-phase composition of the specimen by the usual method of Hanawalt et al.<sup>8</sup> In this connection special care was taken in the following aspect of the problem: viz. detection of the

presence of a new phase other than free ammonium nitrate and ammonium sulphate. It is worthwhile mentioning here that ammonium nitrate exists in five different polymorphic forms; the transition temperature of variety III to IV lies around 32.3°C which is near the room temperature<sup>9</sup>. Their x-ray data are given in Table 2A.

TABLE 2A—X-RAY DATA ON  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  AND DOUBLE SALTS 2 : 1 AND 3 : 1 BY PREVIOUS WORKERS

By Sauchillie*						By James P. Smith <sup>4</sup>			
$(\text{NH}_4)_2\text{SO}_4$		$\text{NH}_4\text{NO}_3\text{-III}$		$\text{NH}_4\text{NO}_3\text{-IV}$		2 : 1		3 : 1	
$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>
5.30	m	5.20	w	4.90	m	10.1	w	12.3	vw
5.20	m	4.49	m	3.93	ms	7.52	w	7.73	w
4.40	vs	3.88	s	3.64	vw	6.70	w	5.37	m
4.30	vs	3.37	m	3.08	s	5.45	w	5.06	m
3.89	s	3.22	ms	2.87	mw	5.22	vw	4.76	s
3.27	vw	3.19	ms	2.71	ms	4.95	s	4.54	m
3.22	vw	2.91	mw	2.48	m	4.68	s	4.14	vw
3.14	ms	2.82	m	2.38	mw	4.17	vw	3.99	w
3.05	s	2.54	vw	2.28	ms	3.87	m	3.80	vw
2.99	m	2.41	m	2.24	ms	3.26	vs	3.63	vw
2.78	mw	2.31	m	2.09	w	3.17	s	3.38	vw
2.70	w	2.27	w	1.97	w	2.92	s	3.25	s
2.66	m	2.26	mm	1.83	w	2.84	ms	3.17	vs
2.52	mw	2.22	mw	1.80	vw	2.65	vw	3.11	w
2.47	vw	2.20	w	1.78	w	2.58	w	2.98	m
2.40	vw	2.08	vvw	1.73	vw	2.47	m	2.89	s
2.37	vw	2.03	vw	1.63	w	2.40	m	2.77	w
2.32	m	1.96	vw	1.58	vw	2.23	mw	2.68	w
2.19	mw	1.92	vw	1.57	w	2.12	m	2.49	m
2.17	m	1.91	vw	1.52	vvw	2.03	w	2.38	vw
2.09	w	1.82	w	1.51	w	1.93	w	2.34	m
2.06	vw	1.77	vw	1.49	w	1.63	w	2.27	w
1.97	w	1.74	w	1.46	w	1.46	w	2.19	ms
1.94	w	1.69	vvw	1.44	vw	1.38	w	2.09	m
1.92	vw	1.66	vvw	1.42	vw	1.36	w	1.99	vw
1.90	vw	1.62	w	1.38	vvw			1.93	vw
1.87	vvw	1.56	w	1.36	w			1.87	vw
1.82	vvw	1.50	vvw	1.33	vw			1.84	vw
1.78	w	1.49	w	1.32	w			1.77	vw
1.73	vvw	1.47	vvw	1.27	vw			1.68	vw
1.70	w	1.46	vw	1.26	vvw			1.65	vw
1.63	w	1.42	vvw	1.21	w			1.62	vw
1.50	w	1.40	vvw	1.18	vvw			1.58	vw
1.42	w							1.46	vw
								1.44	vw
								1.42	vw
								1.38	vw
								1.36	vw

vs—very strong, s—strong, ms—medium strong, m—medium, mw—medium weak, w—weak, vw—very weak, vvw—very very weak

\*Sauchellie, Vincent, Chemistry & Technology of Fertilizers, ACS Monograph Series 148, Reinhold Publishing Corporation, New York (1960)

TABLE 2B—X-RAY DATA ON DOUBLE SALTS 1:1, 2:1, 3:1, PREPARED IN THE LABORATORY, AND MANUFACTURED  
DOUBLE SALT (SINDRI)

1 : 1		2 : 1		3 : 1		Commercial Salt, Sindri	
$d(\text{\AA})$	$I$	$d(\text{\AA})$	$I$	$d(\text{\AA})$	$I$	$d(\text{\AA})$	$I$
6.20	w	5.73	vvw	5.19	w	5.50	vw
5.34	w	5.11	s	5.12	m	4.90	ms
5.13	w	4.67	ms	4.87	s	4.26	s
4.83	s	4.27	vvw	4.12	vw	3.88	vw
4.70	ms	3.82	vvw	3.86	vvw	3.63	vw
4.60	mw	3.45	ms	3.30	s	3.32	s
4.07	vw	3.31	s	3.21	s	3.19	mw
3.90	w	3.20	mw	3.11	vvw	3.08	mw
3.43	mw	3.00	ms	2.99	s	2.93	w
3.28	s	2.89	s	2.83	vw	2.85	vw
3.18	s	2.59	w	2.57	vw	2.50	vw
3.10	vvw	2.39	w	2.41	vw	2.39	s
3.00	vw	2.28	vw	2.24	vw	2.13	vw
2.90	ms	2.16	vvw	2.15	vw	1.96	vw
2.80	vvw	1.96	vw			1.79	vvw
2.64	m	1.81	vvw			1.65	vw
2.51	vvw	1.66	vvw			1.57	vvw
2.44	m	1.51	vw			1.48	vw
2.37	vvw	1.42	vvw			1.44	vw
2.30	vvw	1.39	vw				
2.22	w	1.32	vw				
2.12	vw	1.27	w				
		1.22	vw				
		1.18	vw				

vs—very strong, s—strong, ms—medium strong, m—medium, mw—medium weak, w—weak, vw—very weak, vvw—very very weak

TABLE 3—OPTICAL & X-RAY DATA OF THE PREVIOUS AUTHORS ON 3 : 1, & 2 : 1 DOUBLE SALTS

$\text{NH}_4\text{NO}_3 : (\text{NH}_4)_2\text{SO}_4$	Optical Data			X-ray Data	
	James P. Smith et al <sup>a</sup>	Janecke et al <sup>b</sup>	Thomas & Hallimond <sup>b</sup>	James P. Smith et al <sup>a</sup>	Bragg <sup>b</sup>
3 : 1	Biaxial (—) 2V = 42.50 $n_\alpha = 1.489$ $n_\beta = 1.535$ $n_\gamma = 1.543$		Optically—ve 2E = 80° $n_\alpha = 1.221$ $n_\beta = 1.533$ $n_\gamma = 1.536$	$a = 12.39 \text{\AA}$ $b = 5.95 \text{\AA}$ $c = 9.94 \text{\AA}$ $\beta = 92^\circ 42'$ P2 <sub>1</sub> /m or P2 <sub>1</sub> monoclinic	
2 : 1	Biaxial (—) 2V = 60° $n_\alpha = 1.471$ $n_\beta = 1.531$ $n_\gamma = 1.552$	Birefringence (—) $n_\alpha = 1.519$ $n_\beta = 1.528$ $n_\gamma = 1.536$	2E = 110° $n_\alpha = 1.521$ $n_\beta = 1.531$ $n_\gamma = 1.536$	$a = 10.40 \text{\AA}$ $b = 11.40 \text{\AA}$ $c = 10.31 \text{\AA}$ $\beta = 105^\circ 48'$ P2 <sub>1</sub> /C. Monoclinic	$a = 4.92 \text{\AA}$ $b = 5.88 \text{\AA}$ $c = 10.08 \text{\AA}$ $\alpha = 92^\circ 57'$ $\beta = 82^\circ 11'$ $\gamma = \text{not measured}$ Triclinic

2E = Optical angle in air, 2V = True optic angle,  $a, b, c$  = axial lengths,  $\alpha, \beta, \gamma$  = axial angles.  
 $n_\alpha, n_\beta, n_\gamma$  = refractive indices in three directions.

The x-ray analysis of experimental specimen reveals some interesting results. The powder pattern of the specimen 3:1 double salt in alkaline media gives rise to some lines whose spacings are not in agreement with those of ammonium nitrate and ammonium sulphate (vide Tables 2A & 2B). The values of 'd' spacings of four of such strong lines are 4.87, 3.30, 3.21 and 2.99 Å and these lines are due to 3:1 salt. It is, however, to be noted that the evidence of the presence of free ammonium nitrate has been found in the photograph of the above specimen. The overall content of this phase seems to be small when compared with 3:1 phase. Again, some lines (though comparatively weak) due to ammonium sulphate are also found in the x-ray photograph. Similarly in the diffraction pattern of sample 2:1 salt (prepared in strongly basic media), some new lines corresponding to 'd' values of 5.11, 3.31 and 2.89 Å have been found along with lines due to ammonium sulphate. There is also an indication of the presence of ammonium nitrate as a minor constituent in the above specimen.

So far in the literature there are only two evidences of the existence of 1:1 double salt<sup>1, 10</sup>. A double salt is formed from hot aqueous and alkaline medium of the solution of ammonium nitrate and ammonium sulphate in molecular ratio 4:1, and an x-ray photograph of such a specimen reveals the presence of a number of lines, 'd' spacings of which do not correspond to either of the preceding double salts nor to  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . Three strong lines of the specimen are 4.83, 4.70 and 3.28 Å. Incidentally, it can be pointed out here that a similar phase is also precipitated from the similar hot and neutral solution (not alkaline) with some amount of free ammonium nitrate and ammonium sulphate as is exhibited in the diffraction pattern of such precipitate. Strangely enough,

no such phase viz. 1:1 composition is obtained from cold solution.

In the case of the commercial double salt (Sindri), x-ray diffraction pattern reveals the presence of  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  as distinct separate phases. There are also some lines due to other phases of 'd' values viz. 4.26, 3.32, 2.39 Å (strong lines) etc. and these spacings do not agree with those of the preceding double salts.

Further work on single crystal studies of the above double salts is in progress.

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# Adsorption $(\text{NH}_4)^+$ Ion by Clay from Different Fertilizer Grade Ammonium Compounds

By

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A comparative study on the adsorption of  $(\text{NH}_4)^+$  ions from the different types of nitrogenous fertilizers by clay having varying composition has been made. It has been observed that the adsorption of  $(\text{NH}_4)^+$  ions is maximum from ammonium sulphate, ammonium nitrate sulphate and calcium ammonium nitrate (CAN), while in the case of ammonium nitrate the adsorption is minimum. This paper also gives an account of the adsorption of  $(\text{NH}_4)^+$  ions from ammonium nitrate system with varying content of ammonium sulphate and calcium nitrate.

## Introduction

The fixation of nitrogen in soil is a time-old problem of fertilizer technology. It is generally believed that the capacity of soil to produce crops is directly related to the amount of plant nutrients which it retains. As a matter of fact, soil can be considered as a huge storehouse for plant nutrients. Whenever a fertilizer is added to the soil, the nutrient is fixed on the soil colloid by an ion-exchange process; soils with a relatively high ion-exchange capacity are fertile. The base-exchange capacity (B.e.c.) of the soil is, however, dependent on a number of factors, like (i) the nature and types of associated minerals and organic matter, (ii) the nature of the clay minerals and their state of aggregation, (iii) concentration and the nature of the exchanging and the exchangeable ions, (iv) the temperature and pH of the system, etc. Of these factors, clay particles contribute a major portion in the adsorption process. Obviously the role of the different types of nitrogenous fertilizers on the adsorption of  $(\text{NH}_4)^+$  ions by diverse types of clay of high base-exchange capacity proposes an interesting topic of research from the technological point of view of fertilizer industry. Recently, an interesting report has been published to that end by Japanese workers, who found that in the case of ammonium nitrate the  $(\text{NH}_4)^+$  ion retention of Takachi volcanic ash soil is weaker than while using ammonium sulphate in the top soil<sup>1</sup>.  $(\text{NH}_4)^+$  ion is fixed readily by clay particles, hydrated oxides of iron and aluminium and organic matter present in the soil, which are not leached out by rain or drainage from the soil. Since a major amount of  $(\text{NH}_4)^+$  ion is absorbed by clay, it will be

interesting to know the relative adsorption of  $(\text{NH}_4)^+$  ion by clay minerals of high base-exchange capacity, like montmorillonite, which is very often associated with soil, from diverse nitrogenous fertilizers like ammonium nitrate, ammonium sulphate, ammonium acetate, ammonium nitrate sulphate and calcium ammonium nitrate (CAN). The representative clay samples used in the present investigation are Tinpahari, Rajasthan and Kashmir bentonites.

## Experimental

All the ammonium compounds used in the investigation were of A.R.\* quality, except the double salt  $[(\text{NH}_4)_2\text{SO}_4 \text{ and } \text{NH}_4\text{NO}_3 \text{ in } 3:2 \text{ ratio by wt.}]$  and CAN—a mixture of limestone and ammonium nitrate in 2:3 ratio by weight—which were obtained from Sindri and Nangal Units of F.C.I. Ltd. respectively. Approximately 1 N solution of an ammonium compound was prepared (in case of CAN, calculation was made on the basis of ammonium nitrate content). To about 1 g. of clay approximately 20 ml. solution was added, shaken by hand and kept overnight. The pH of the solution was adjusted to 7 by adding dilute ammonia. This was done because adsorption depends on the pH of the solution as mentioned earlier.

Then the supernatant liquid was siphoned off and again 20 ml. of solution was added, shaken for some time and allowed to settle. This was repeated for two or three times. The sediment was then washed with distilled water and finally with A.R. quality methyl

\* Analytical Reagent

alcohol by centrifuge till free from added salt.  $(\text{NH}_4)^+$  on adsorbed by clay was determined by distilling the sample with caustic soda and absorbing the ammonia as by known quantity of N/20 sulphuric acid, the excess acid being titrated with standard potassium hydroxide using phenolphthalein as an indicator.

The identification of crystalline phase by x-ray analysis was made by the usual standard method, and some results were correlated with D.T.A.<sup>2,3</sup>. The x-ray apparatus used was of Russian type,  $\bar{\Lambda}$  P-3. Nickel filtered  $\text{CuK}\alpha$  radiation, generated at 30 KV, and 20 mA was used. Cylindrical camera of 5.72 cm. diameter was used for this investigation.

## Discussion

The physical characteristics of those clay samples with particular reference to their composition were revealed by x-ray diffraction analysis and D.T.A. thermogram (Table 1; and Fig. 1). Montmorillonite was found to be the only constituent in Tinpahari bentonite. A very small amount of other minerals like haematite, rutile and hydrobiotite was detected in the coarser grains (about  $5\mu$  size) of Tinpahari bentonite<sup>4</sup>. Rajasthan bentonite was found to contain montmorillonite only, while Kashmir bentonite was a mixture of montmorillonite and kaolinite.

The base-exchange capacity data of different clays (Table 2) reveal two interesting results, viz. the adsorption of  $(\text{NH}_4)^+$  ion by clay is related to the nature of ammonium compound as well as the clay mineral. In the present investigation, the adsorption of  $(\text{NH}_4)^+$  ion is maximum in the case of Tinpahari bentonite, irrespective of the nature of ammonium compound used. The corresponding adsorption data in the case of Rajasthan bentonite are slightly less, while data from Kashmir bentonite show a marked contrast—the adsorption of  $(\text{NH}_4)^+$  ions is very small. Adsorption in usual unit, viz. m. eq./100 g., from ammonium sulphate by different bentonites is as follows: Tinpahari bentonite (78.7), Rajasthan bentonite (75.8) and Kashmir bentonite (18.76). Similar variation has been observed in the case of other ammonium compounds studied in this laboratory. A possible cause for this observation can be related to the crystal-phase composition of bentonite. The low value of  $(\text{NH}_4)^+$  ion adsorption of Kashmir bentonite can be accounted for by the presence of kaolinite.

Again critical study of base-exchange capacity data reveals that the adsorption of  $(\text{NH}_4)^+$  ion by the same clay specimen varies with the nature of the ammonium

TABLE 1—X-RAY DATA OF BENTONITE SAMPLES

Tinpahari		Rajasthan		Kashmir	
Intensity	Spacing (d) Å	Intensity	Spacing (d) Å	Intensity	Spacing (d) Å
vs	14.87(M)	vs	14.12(M)	s	14.02(M)
vw	5.02	m	4.48(M)	s	7.19(k)
s	4.46(M)	w	3.17	m	4.45(M)
vw	3.58	m	2.57	s	3.56(k)
vw	3.15	vw	1.90	m	2.55
vw	2.80	vw	1.71	s	2.35(k)
m	2.61	m	1.51(M)	vw	2.12
w	1.73	vw	1.30	vw	2.01
s	1.52(M)	vw	1.26	w	1.68
w	1.31			s	1.49(M)
vw	1.26				

vs = very strong  
s = strong  
m = medium  
w = weak  
vw = very weak  
M = montmorillonite  
k = Kaolinite

Glycerol-treated samples of Tinpahari, Rajasthan and Kashmir Bentonites show a spacing at 17.72, 17.5 and 17.7 Å respectively.

TABLE 2—BASE EXCHANGE CAPACITY OF BENTONITE SAMPLES

Base Exchange Reagent	Tinpahari Bentonite, m.eq/100 g	Rajasthan Bentonite, m.eq/100 g	Kashmir Bentonite, m.eq/100 g
$\text{CH}_3\text{COO NH}_4$	75.43	74.52	17.01
$\text{NH}_4\text{NO}_3$	74.0	58.35	16.36
$(\text{NH}_4)_2\text{SO}_4$	78.7	75.8	18.76
Double Salt (Ammonium Sul- phate Nitrate)	77.38	75.63	18.05
CAN (Calcium Ammonium Nitrate)	78.63	70.63	17.02

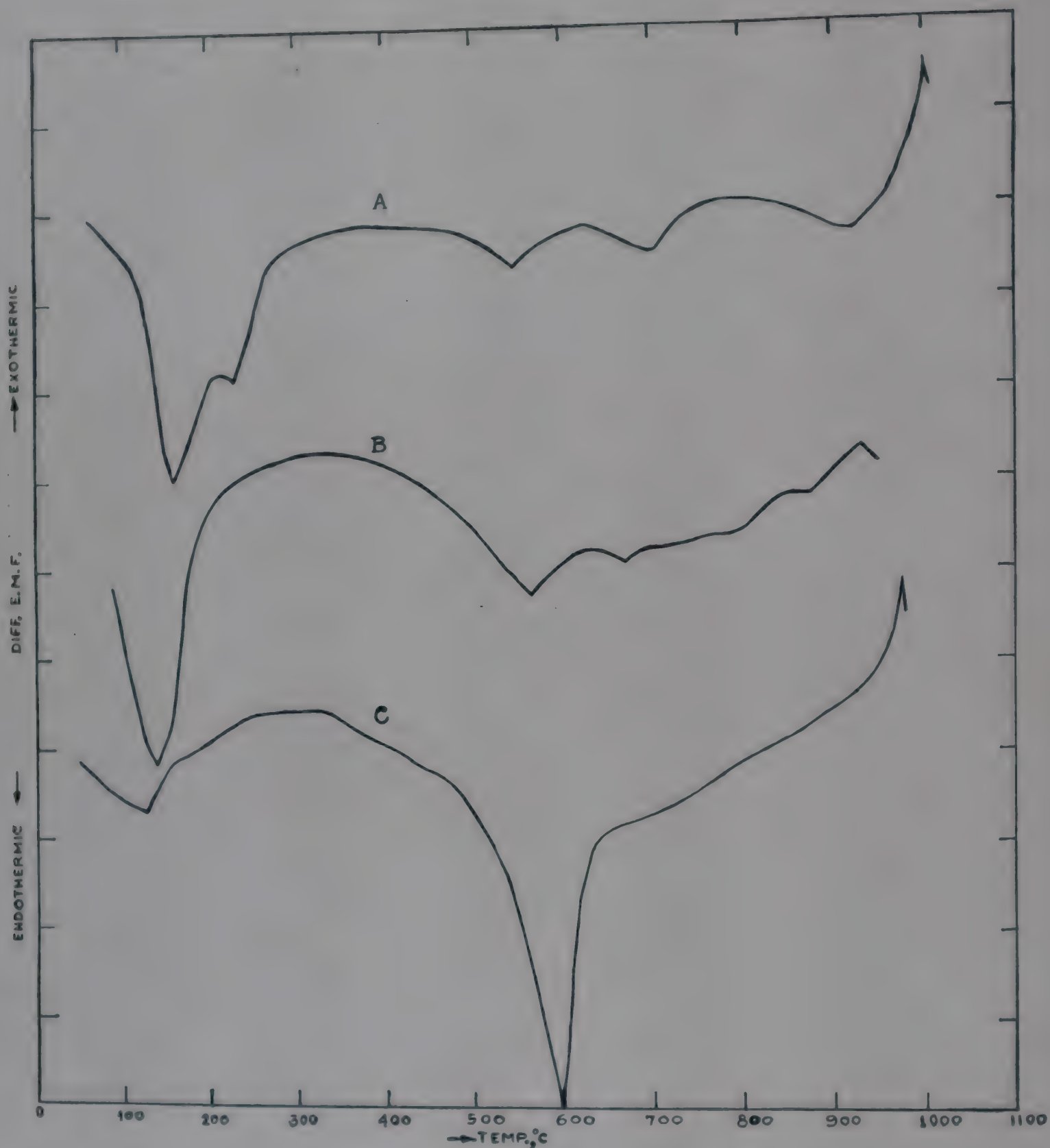


Fig. 1. D.T.A. Thermograms of Bentonites.

- A. Tinpahari Bentonite.
- B. Rajasthan "
- C. Kashmir "

compound, e.g. the adsorption data of ammonium sulphate can be compared with that of ammonium nitrate (74.0) in Tinpahari bentonite (Table 2). The corresponding data for ammonium nitrate sulphate, calcium ammonium nitrate and ammonium acetate are 77.38, 78.63 and 75.43 respectively. Similar variation in

the nature of  $(\text{NH}_4)^+$  ion adsorption is also evident in other two clay samples.

Again, it has been observed that the addition of ammonium sulphate in ammonium nitrate up to 1.22 per cent increased the adsorption value up to 90.1 m.eq./100 g. in case of Tinpahari bentonite (Table 3,

Fig. 2). On further addition, this value decreases and remains fairly constant at higher percentage of ammonium sulphate. The high adsorption value at optimum ( $\text{SO}_4$ )<sup>''</sup> ion concentration may be accounted for by the removal of the maximum amount of  $\text{Ca}^{++}$  ion from the clay surface in the form of insoluble calcium sulphate. The appearance of double peaks in the initial endothermic reaction in the D.T.A. curve of this sample confirms the presence of adsorbed  $\text{Ca}^{++}$  ions (Fig. 1).

TABLE 3—BASE EXCHANGE CAPACITY (B.E.C.) OF TINPAHARI BENTONITE IN DIFFERENT  $\text{NH}_4\text{NO}_3$  AND  $(\text{NH}_4)_2\text{SO}_4$  COMPOSITIONS

$(\text{NH}_4)_2\text{SO}_4$ in mixtures, %	B.e.c., m.eq/100 g.
0.00	74.0
1.22	90.1
3.96	85.0
9.35	84.2
20.0	79.32
25.0	78.79
33.3	78.77
50.0	77.38

TABLE 4—BASE EXCHANGE CAPACITY (B.E.C.) OF TINPAHARI BENTONITE IN DIFFERENT  $\text{NH}_4\text{NO}_3$  AND  $\text{Ca}(\text{NO}_3)_2$  COMPOSITIONS

$\text{Ca}(\text{NO}_3)_2$ in mixture, %	B.e.c., m.eq/100 g.
0.00	74.0
6.35	73.9
8.10	75.7
13.0	77.0
16.9	66.4
30.6	65.6

The adsorption of  $(\text{NH}_4)^+$  ion is perhaps suppressed at higher concentration of  $(\text{SO}_4)''$  ions in the mixture.

It is evident that the effect of the varying concentration of calcium nitrate in a system  $\text{NH}_4\text{NO}_3$ — $\text{Ca}(\text{NO}_3)_2$  on the adsorption behaviour of Tinpahari bentonite is similar to that of  $\text{NH}_4\text{NO}_3$ — $(\text{NH}_4)_2\text{SO}_4$  system, but unlike the latter, adsorption of  $(\text{NH}_4)$  ion increases slightly up to a certain concentration of  $\text{Ca}(\text{NO}_3)_2$  (Table 4, Fig. 2) in  $\text{NH}_4\text{NO}_3$ — $\text{Ca}(\text{NO}_3)_2$  system the optimum adsorption value (77.0) being observed corresponding to 13.0 per cent of  $\text{Ca}(\text{NO}_3)_2$  in

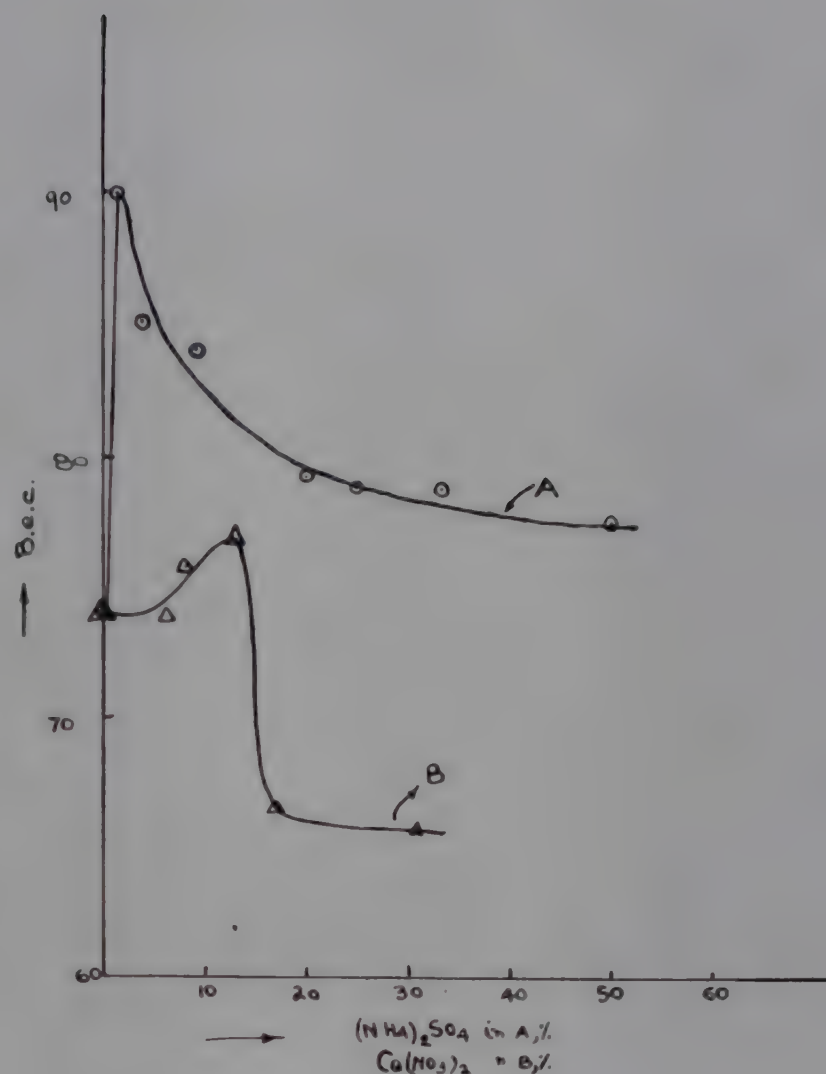


Fig. 2. Adsorption Characteristics of  $(\text{NH}_4)^+$  Ion by Clay from  $(\text{NH}_4)\text{NO}_3$  System containing  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Ca}(\text{NO}_3)_2$ .

A. Mixture of  $(\text{NH}_4)_2\text{SO}_4$  &  $\text{NH}_4\text{NO}_3$ .  
B. Mixture „  $\text{Ca}(\text{NO}_3)_2$  &  $\text{NH}_4\text{NO}_3$ .

the mixture. The solution of calcium ammonium nitrate used has a concentration of 6.26 per cent  $\text{Ca}(\text{NO}_3)_2$ —in terms of mixture of  $\text{NH}_4\text{NO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ —which is in the zone of optimum adsorption value studied (Fig. 2).

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# Efficiency of Various Forms of Phosphate in Crop Plant Nutrition

## PART I—RESPONSE OF *AUS* PADDY IN POT CULTURES

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A comparison on the effects of the four sources of phosphorus, viz. calcined phosphate, fused calcium magnesium phosphate, mulitphosphate and superphosphate, on the growth and composition of *Aus* paddy in pot culture has been made. The fertilizers were applied as basal dressing.

The plants receiving multiphosphate indicated a more rapid growth in terms of height, thickness of stem, leaf area and dry weight. The percentage utilization of the phosphorus supplied and the uptake of nitrogen and potassium were higher in the plants which were given multiphosphate.

### Introduction

Phosphorus plays a vital role in crop plant nutrition, the recognition of which has led to an increasing use of fertilizers containing this nutrient. Among the phosphatic fertilizers produced commercially, some contain their available phosphate in a form insoluble in water but soluble in ammonium citrate or citric acid, while others have their available phosphates partly or wholly soluble in water. Divergent views have been expressed in regard to the relative efficiency of these phosphatic fertilizers having different levels of water solubility.<sup>1-8</sup>

Thermal phosphates, insoluble in water but soluble in ammonium citrate or citric acid, have been used successfully in countries like the U.S.A., Japan, Germany and Taiwan, and particularly in Japan they have gained increasing popularity. Among the phosphatic fertilizers, prepared by thermal methods, mention may be made of Rhenania phosphate<sup>9</sup>, fused calcium magnesium phosphate,<sup>10, 11</sup> defluorinated calcined phosphate<sup>12</sup> and fused tricalcium phosphate<sup>13</sup>. India has no experience on the use of such fertilizers. Unlike superphosphate and ammonium phosphate, the manufacture of these fertilizers does not involve the use of sulphur, which is imported in this country. Hence a

study on the efficiency of these fertilizers would be useful.

The present investigation was undertaken with this end in view using the following three thermal phosphates: Fused calcium magnesium phosphate, defluorinated calcined phosphate and multiphosphate. Of these, the method of preparation of the last one is the same as that of the defluorinated calcined phosphate, except that some liquid phosphate is added to the charge before calcination, so that the final product contains some of the available phosphate in a water-soluble form. The relative efficiency of these three thermal phosphates has been compared with that of superphosphate on the growth and development of *Aus* paddy in pot cultures. The results are reported in this paper.

### EXPERIMENTAL

#### Analytical Methods

For the determination of N, P and K in the plant material, the microdigestion method of Yuen and Pollard<sup>14</sup> has been used. For the phosphate in the plant material, the molybdenum blue-amino-naphthol sulphonic acid method of Yuen and Pollard<sup>15</sup> has been

used. Total nitrogen was determined by the Nessler's method as modified by Yuen and Pollard.<sup>16</sup> The methods used for the various other estimations were those described by Piper.<sup>17</sup>

### Pot Culture Methods

The general character of the two soils used, viz. those of the Indian Agricultural Research Institute at Delhi and Sindri farm, are given in Table 1. The test crop used was 'Dhairal' variety of *Aus* paddy.

Out of the four fertilizers studied in the present experiment, calcined phosphate and multiphosphate samples were supplied by the Onado Fertilizer Company of Japan, and the fused phosphate samples by Hinode Gagaku Kogvo K. K. Company, also of Japan. Superphosphate was supplied by one of the local factories. The nutrient contents of the fertilizers are given in Table 2.

The fertilizers were applied in three levels, viz. 50, 100 and 200 lbs of  $P_2O_5$  per acre. Since there were three levels of application and four different fertilizer treatments including the control, a randomised block design with two replicas was adopted for each set of soil.

TABLE 1—ANALYSES OF SOIL SAMPLES (ON OVEN DRY BASIS)

	Location	
	I.A.R.I, Delhi (Top block)	Sindri Farm
(a) Mechanical Analysis, %		
Clay .. ..	15.23	21.90
Silt .. ..	11.07	20.48
Sand .. ..	69.22	53.76
(b) Chemical Analysis		
1. Organic Carbon, %	0.312	0.822
2. Total Nitrogen, %	0.076	0.119
3. Total $P_2O_5$ , %	0.065	0.106
4. Total Potash ( $K_2O$ ), %	0.578	0.964
5. pH	7.95	7.80
6. B.E.C., m. eq./100 g. of soil	8.37	13.72
7. Exchangeable bases, m. eq./100 g. soil		
(a) Exchangeable $K^+$	0.332	0.388
(b) -do- $Ca^{++}$	3.250	2.400
(c) -do- $Na^+$	0.196	0.224

B.E.C. = Base Exchange Capacity

TABLE 2—NUTRIENT CONTENTS OF THE PHOSPHATE FERTILIZERS

Fertilizer	Manufacturer	Total $P_2O_5$ , %	Citrate Soluble $P_2O_5$ , %	Water Soluble $P_2O_5$ , %
Calcined Phosphate	Onoda Fertilizer Co., Japan	39.44	30.24	Nil
Multiphosphate	-do-	29.09	22.53	20.49
Fused phosphate	Hinode Gagaku Kogvo K. K. Co., Japan	22.01	19.64	Nil
Super phosphate	Local	16.50	16.50	16.00

### Procedure

All the earthen pots were coated properly with black bitumen paint and one kilogram of 2 mm. air-dry soil was weighed in each pot, the soil surface being 2" below the top level of the pot.

The treatments within each block were randomised individually. In this experiment, there were fifty-two pots altogether, with each block containing thirteen pots.

The different fertilizers were weighed accurately and mixed intimately with the soils of the respective pots before sowing. The total amount of phosphate applied was as below:

No.	Abbreviations	Phosphate Fertilizers	Lbs/acre of $P_2O_5$	Mg $P_2O_5$ /Pot
1.	Control	—	0	0
2.	C <sub>1</sub>	Multiphosphate	50	25
3.	C <sub>2</sub>	Multiphosphate	100	50
4.	C <sub>3</sub>	Multiphosphate	200	100
5.	F <sub>1</sub>	Fused Phosphate	50	25
6.	F <sub>2</sub>	Fused Phosphate	100	25
7.	F <sub>3</sub>	Fused Phosphate	200	100
8.	M <sub>1</sub>	Calcined phosphate	50	25
9.	M <sub>2</sub>	Calcined phosphate	100	50
10.	M <sub>3</sub>	Calcined phosphate	200	100
11.	S <sub>1</sub>	Superphosphate	50	25
12.	S <sub>2</sub>	Superphosphate	100	50
13.	S <sub>3</sub>	Superphosphate	200	100

On 10-4-64, six seeds were sown in each pot and all the pots were then irrigated with same quantity of distilled water. Germination was completed by 14-4-64, when the seedlings were thinned to 4 per pot.

At the end of each week, the blocks were rotated and interchanged amongst themselves, keeping the randomisation within each block intact to ensure equal light and temperature to all the pots. The temperature of the small green house was around 90°F during the experiment. Fifty millilitres of distilled water were applied every day to each pot. The height of each plant from the soil surface to the tip of the last leaf was measured periodically.

In order to determine the dry matter yield and the nutrient status at the peak period of their vegetative growth, the rice plants were harvested on 1-6-64. The tops and roots were separated, dried, weighed and analysed.

## RESULTS AND DISCUSSION

### Effect of Different Fertilizers on the Growth and Development of Rice Plants

The morphological differences due to the different treatments began to show in about 21 days after the emergence of the rice plants. These were considerable in the pots receiving the third and second level treatments. The calcined phosphate treated plants turned yellow after 12 days of emergence from which they recovered at the later stages of growth.

At the 5 per cent level of significance, the statistical interpretation of the height measurement results is as follows:

#### (a) I.A.R.I. Soil (Table 3)

\*C<sub>2</sub> S<sub>3</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>1</sub> F<sub>1</sub> M<sub>1</sub> S<sub>3</sub> F<sub>3</sub> M<sub>3</sub> C<sub>3</sub> Control

#### (b) Sindri Soil (Table 3).

S<sub>3</sub> C<sub>3</sub> F<sub>3</sub> M<sub>3</sub> C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> F<sub>1</sub> C<sub>1</sub> S<sub>1</sub> M<sub>1</sub> Control

It is interesting to note that in the I.A.R.I. soil, the third-level treated plants did not respond to the application of phosphate, probably because of phosphate

\* (1) The treatments are arranged in order of their respective merits (highest to lowest)

(2) Treatments within the same bar indicate that the observed differences between the treatment are due to chance.

TABLE 3—HEIGHT OF RICE PLANTS

(Each Figure Represents an Average of Eight Heights)

Treatments	I.A.R.I. Soil Height, mm	Sindri Soil Height, mm
Control	18.25	27.15
C <sub>1</sub>	25.90	30.75
C <sub>2</sub>	29.80	32.85
C <sub>3</sub>	18.95	36.15
F <sub>1</sub>	23.95	31.20
F <sub>2</sub>	27.10	31.90
F <sub>3</sub>	20.75	34.35
M <sub>1</sub>	23.25	29.80
M <sub>2</sub>	26.75	31.25
M <sub>3</sub>	20.65	33.90
S <sub>1</sub>	24.95	30.00
S <sub>2</sub>	28.50	32.05
S <sub>3</sub>	20.95	36.60
'F' Value of the treatments	141.22***	71.15***
'F' Value of the blocks	0.015	1.438
C.D. at the 5 per cent level	0.8969	0.8954

\*\*\* Significant at the 0.1% level

C.D. = Critical Difference

'F' = Variance ratio value

toxicity. However, it can be concluded from the above interpretation that multiphosphate and superphosphate are much more efficient in encouraging vegetative growth than are fused phosphate and calcined phosphate.

### Dry Matter Yields of Rice Tops

Statistical analysis of the results showed that the observed variations due to the treatments are significant at 0.1 per cent level. At the 5 per cent level, the statistical interpretation of the results is as follows:

#### (a) I.A.R.I. Soil (Table 4)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>1</sub> F<sub>1</sub> M<sub>1</sub> M<sub>3</sub> S<sub>3</sub> C<sub>3</sub> F<sub>3</sub> Control

#### (b) Sindri Soil (Table 4).

S<sub>3</sub> C<sub>3</sub> F<sub>3</sub> M<sub>3</sub> S<sub>2</sub> C<sub>2</sub> F<sub>2</sub> M<sub>2</sub> S<sub>1</sub> F<sub>1</sub> C<sub>1</sub> M<sub>1</sub> Control

The yield of rice tops in Sindri soil was much more than in the case of I.A.R.I. soil, which confirms the poor nutrient status of the I.A.R.I. soil. In the I.A.R.I. soil, the third level treated plants failed to respond to the various phosphatic fertilizers probably because

of phosphate toxicity resulting from the unbalanced lower uptake of the other nutrients. In general, multi-phosphate in the I.A.R.I. soil and superphosphate and multiphosphate in Sindri soil produced higher dry matter yields than in the case of the other fertilizer treatments.

### Dry Matter Yield of Rice Roots

Statistical analysis of the results affords the following interpretation at the 5 per cent level:

#### (a) I.A.R.I. Soil (Table 4)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> F<sub>1</sub> M<sub>1</sub> S<sub>1</sub> F<sub>3</sub> C<sub>3</sub> S<sub>3</sub> M<sub>3</sub> Control

#### (b) Sindri Soil (Table 4)

C<sub>3</sub> S<sub>3</sub> F<sub>3</sub> M<sub>3</sub> C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> S<sub>1</sub> M<sub>2</sub> C<sub>1</sub> M<sub>1</sub> Control F<sub>1</sub>

The dry matter yields of the roots apparently follow the same trend as those of the tops.

### Uptake of Phosphate by Rice Plants

#### (i) Rice Tops

Table 5 records the total uptake of P<sub>2</sub>O<sub>5</sub> by rice tops. The observed variations due to the treatments are significant and the interpretation at the 5 per cent level is as follows:

#### (a) I.A.R.I. Soil

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>3</sub> S<sub>1</sub> M<sub>1</sub> M<sub>3</sub> F<sub>1</sub> C<sub>3</sub> F<sub>3</sub> Control

The total P<sub>2</sub>O<sub>5</sub> uptake of C<sub>2</sub> plants was 20.54, 24.08, 65.12 and 366.66 per cent above those of S<sub>2</sub>, F<sub>2</sub>, M<sub>2</sub> and control plants respectively.

The P<sub>2</sub>O<sub>5</sub> uptake of C<sub>1</sub> plants was respectively 6.98, 16.26, 23.71 and 114.49 per cent higher than those of the S<sub>1</sub>, M<sub>1</sub>, F<sub>1</sub> and Control.

#### (b) Sindri Soil

C<sub>3</sub> C<sub>2</sub> F<sub>3</sub> M<sub>3</sub> M<sub>2</sub> S<sub>3</sub> F<sub>1</sub> S<sub>1</sub> S<sub>2</sub> F<sub>2</sub> C<sub>1</sub> M<sub>1</sub> Control

The total P<sub>2</sub>O<sub>5</sub> content of the C<sub>3</sub> tops was respectively 27.86, 28.83, 49.01 and 101.37 per cent above those of F<sub>3</sub>, M<sub>3</sub>, S<sub>3</sub> and Control.

In C<sub>2</sub> plants, values were 13.94, 44.76, 55.70 and 75.12 per cent greater than those of the M<sub>2</sub>, S<sub>2</sub>, F<sub>2</sub> and control plants respectively.

#### (ii) Rice Roots

Variations in the uptake at P<sub>2</sub>O<sub>5</sub> due to the different treatments are significant at 0.1 per cent level and the statistical interpretation of the results at the 5 per cent level is as follows:

#### (a) I.A.R.I. Soil (Table 5)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> F<sub>3</sub> S<sub>1</sub> C<sub>3</sub> M<sub>1</sub> M<sub>3</sub> F<sub>1</sub> C<sub>1</sub> S<sub>3</sub> Control

The uptake of P<sub>2</sub>O<sub>5</sub> by C<sub>2</sub> roots was 3.24, 22.73, 31.33 and 286.83 per cent respectively above those of the S<sub>2</sub>, F<sub>2</sub>, M<sub>2</sub> and control roots.

#### (b) Sindri Soil (Table 5)

C<sub>3</sub> S<sub>3</sub> C<sub>2</sub> F<sub>3</sub> S<sub>1</sub> F<sub>2</sub> C<sub>1</sub> M<sub>3</sub> M<sub>2</sub> S<sub>2</sub> F<sub>1</sub> Control M<sub>1</sub>

TABLE 4—DRY MATTER YIELD OF RICE PLANTS, g.

(Each Figure Represents an Average of Two Replicates)

Treatments	I.A.R.I. Soil		Sindri Soil	
	Rice Tops	Rice Roots	Rice Tops	Rice Roots
Control	.211	.145	1.408	1.432
C <sub>1</sub>	.415	.320	1.595	1.567
C <sub>2</sub>	.876	.607	1.808	1.801
C <sub>3</sub>	.255	.222	2.341	2.171
F <sub>1</sub>	.362	.299	1.598	1.358
F <sub>2</sub>	.654	.429	1.715	1.723
F <sub>3</sub>	.220	.238	2.153	1.906
M <sub>1</sub>	.346	.296	1.502	1.501
M <sub>2</sub>	.597	.401	1.700	1.644
M <sub>3</sub>	.306	.200	1.979	1.899
S <sub>1</sub>	.392	.287	1.658	1.648
S <sub>2</sub>	.726	.509	1.873	1.769
S <sub>3</sub>	.301	.207	2.394	2.094
'F' value of the treatments	887***	295***	276***	44***
'F' value of the blocks	1.00	.08	2.86	0.28
C.D. at the 5% level	0.0203	.0221	.0536	0.1054

\*\*\* Significant at the 0.1% level.

C<sub>3</sub> treated roots showed an uptake of P<sub>2</sub>O<sub>5</sub> respectively 10.68, 16.19, 33.24 and 82.88 per cent above those of the S<sub>3</sub>, F<sub>3</sub>, M<sub>3</sub> and control roots. C<sub>2</sub> plants had a P<sub>2</sub>O<sub>5</sub> uptake 10.83, 16.12, 19.74 and 57.15 per cent respectively greater than those of F<sub>2</sub>, M<sub>2</sub>, S<sub>2</sub> and control roots.

(iii) *Uptake of Phosphorus Pentoxide by Whole Rice Plants (Tops+Roots)*

Table 5 gives a summary of the total uptake of P<sub>2</sub>O<sub>5</sub> by the rice plants. Variations due to the treatments are significant at 0.1 per cent level. The statistical interpretation of the results at the 5 per cent is as follows:

(a) I.A.R.I. Soil

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>1</sub> S<sub>3</sub> M<sub>1</sub> M<sub>3</sub> F<sub>1</sub> C<sub>3</sub> F<sub>3</sub> Control

(b) Sindri Soil

C<sub>3</sub> C<sub>2</sub> F<sub>3</sub> S<sub>3</sub> M<sub>3</sub> M<sub>2</sub> S<sub>1</sub> F<sub>1</sub> F<sub>2</sub> S<sub>2</sub> C<sub>1</sub> M<sub>1</sub> Control

**Percentage Utilization of Fertilizer Phosphorus**

In different fertilizer treatments, the utilization of the P<sub>2</sub>O<sub>5</sub> actually supplied was calculated by compensating for the uptake of P<sub>2</sub>O<sub>5</sub> by the control plants.

(a) I.A.R.I. Soil: (i) C<sub>2</sub>-treated plants utilized 23.17 per cent of the total P<sub>2</sub>O<sub>5</sub> supplied, whereas S<sub>2</sub>, F<sub>2</sub> and M<sub>2</sub> plants utilized 18.62, 17.42 and 12.07 per cent respectively.

(ii) C<sub>1</sub>-plants utilized 14.12 per cent as against 13.36, 11.13, and 5.89 per cent of P<sub>2</sub>O<sub>5</sub> utilized by S<sub>1</sub>, M<sub>1</sub> and F<sub>1</sub> plants respectively.

(b) Sindri Soil

(i) C<sub>3</sub>-plants utilized 21.21 per cent of the total P<sub>2</sub>O<sub>5</sub> supplied, whereas, F<sub>3</sub>, S<sub>3</sub> and M<sub>3</sub> plants utilized 13.20, 11.60 and 10.76 per cent respectively.

(ii) C<sub>2</sub>-plants utilized 30.56 per cent whereas M<sub>2</sub>, F<sub>2</sub> and S<sub>2</sub> plants utilized 20.57, 12.49 and 12.03 per cent respectively of P<sub>2</sub>O<sub>5</sub> supplied to them.

(iii) S<sub>1</sub> plants utilized 35.74 per cent of the total P<sub>2</sub>O<sub>5</sub> supplied, whereas, F<sub>1</sub>, C<sub>1</sub> and M<sub>1</sub> plants utilized 26.36, 19.01, and 1.52 per cent respectively.

In both the soil types, multiphosphate treatments (except in the C<sub>1</sub> treatments of Sindri soil) resulted in higher utilization of P<sub>2</sub>O<sub>5</sub> as compared with the corresponding superphosphate, calcined phosphate and fused phosphate treatments. This higher utilization of P<sub>2</sub>O<sub>5</sub>

TABLE 5—UPTAKE OF P<sub>2</sub>O<sub>5</sub> BY THE RICE PLANTS, mg.  
(Each Figure Represents an Average of Two Replicates)

Treatments	I.A.R.I. Soil			Sindri Soil		
	Rice Tops	Rice Roots	Total Uptake (Tops+Roots)	Rice Tops	Rice Roots	Total Uptake (Tops+Roots)
Control	2.6725	0.5095	3.2720	11.6205	11.4560	23.0765
C <sub>1</sub>	5.9210	0.8115	6.8025	12.1540	15.6750	27.8290
C <sub>2</sub>	12.8845	1.9730	14.8575	20.3460	18.0100	38.3560
C <sub>3</sub>	4.1825	1.0280	5.2105	23.4050	20.8850	44.2900
F <sub>1</sub>	4.8465	0.8985	5.7450	15.0690	14.5985	29.6675
F <sub>2</sub>	10.3790	1.6070	11.9860	13.0680	16.2475	29.3155
F <sub>3</sub>	3.1065	1.2520	4.3585	18.3010	17.9735	36.2730
M <sub>1</sub>	5.0935	0.9620	6.0555	12.0200	11.4375	23.4575
M <sub>2</sub>	7.8035	1.5035	9.3070	17.8555	15.5075	33.3630
M <sub>3</sub>	4.8640	0.9240	5.7880	18.1665	15.6705	33.8370
S <sub>1</sub>	5.5350	1.0780	6.6130	14.7065	17.3040	32.0105
S <sub>2</sub>	10.6720	1.9110	12.5830	14.0515	15.0410	29.0925
S <sub>3</sub>	5.6440	0.8280	6.4720	15.7080	18.9715	34.6795
'F' value of the treatments	614.8***	241.1***	857.2***	325.6***	100.7***	200.9***
'F' value of the blocks.	0.403	.031	0.509	2.046	0.547	.040
C.D. at the 5 per cent level.	0.3585	.016	0.3427	0.5660	0.7732	1.1884

\*\*\* Significant at the 0.1% level.

probably explains the higher dry matter yields produced by the multiphosphate treated plants.

#### Uptake of Nitrogen by the Rice Plants

At the 5 per cent level of significance, the interpretations of the results are as follows:

##### Rice Tops

(a) I.A.R.I. (Table 6)

C<sub>2</sub> S<sub>2</sub> M<sub>2</sub> F<sub>2</sub> C<sub>1</sub> S<sub>3</sub> S<sub>1</sub> M<sub>1</sub> M<sub>3</sub> C<sub>3</sub> F<sub>1</sub> F<sub>3</sub> Control

(b) Sindri Soil (Table 6)

C<sub>3</sub> S<sub>3</sub> F<sub>3</sub> M<sub>3</sub> C<sub>2</sub> F<sub>1</sub> S<sub>2</sub> F<sub>2</sub> C<sub>1</sub> M<sub>2</sub> S<sub>1</sub> M<sub>1</sub> Control

##### Rice Roots

(a) I.A.R.I. Soil (Table 6)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> C<sub>3</sub> M<sub>1</sub> S<sub>1</sub> F<sub>3</sub> F<sub>1</sub> M<sub>3</sub> S<sub>3</sub> Control

(b) Sindri Soil (Table 6)

F<sub>3</sub> S<sub>3</sub> C<sub>3</sub> F<sub>1</sub> Control M<sub>3</sub> F<sub>2</sub> C<sub>2</sub> S<sub>1</sub> M<sub>2</sub> C<sub>1</sub> S<sub>2</sub> M<sub>1</sub>

#### Total N Uptake of the Whole Rice Plants (Tops+Roots)

(a) I.A.R.I. Soil (Table 6)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>1</sub> C<sub>3</sub> M<sub>1</sub> S<sub>3</sub> M<sub>3</sub> F<sub>1</sub> F<sub>3</sub> Control

(b) Sindri soil (Table 6)

C<sub>3</sub> S<sub>3</sub> M<sub>3</sub> F<sub>1</sub> C<sub>2</sub> F<sub>3</sub> F<sub>2</sub> C<sub>1</sub> S<sub>2</sub> M<sub>2</sub> S<sub>1</sub> Control M<sub>1</sub>

In both the soil types multiphosphate treated plants utilized the highest amounts of native N as compared with the three other fertilizer treatments.

#### Uptake of Potassium (K) by the Rice Plants

At the 5 per cent level of significance the data yielded the following conclusions:

##### Rice Tops

(a) I.A.R.I. Soil (Table 7)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>1</sub> F<sub>1</sub> S<sub>3</sub> M<sub>3</sub> M<sub>1</sub> C<sub>3</sub> F<sub>3</sub> Control

(b) Sindri Soil (Table 7)

S<sub>3</sub> F<sub>3</sub> M<sub>3</sub> C<sub>3</sub> S<sub>2</sub> S<sub>1</sub> M<sub>2</sub> C<sub>2</sub> F<sub>1</sub> C<sub>1</sub> F<sub>2</sub> M<sub>1</sub> Control

##### Rice Roots

(a) A.I.R.I. Soil (Table 7)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> S<sub>1</sub> M<sub>1</sub> C<sub>1</sub> F<sub>3</sub> F<sub>1</sub> M<sub>3</sub> S<sub>3</sub> C<sub>3</sub> Control

TABLE 6—UPTAKE OF NITROGEN BY RICE PLANTS, MG.  
(Each Figure Represents an Average of Two Replicates)

Treatments	I.A.R.I. Soil			Sindri Soil		
	Rice Tops	Rice Roots	Total Uptake (Tops+Roots)	Rice Tops	Rice Roots	Total Uptake (Tops+Roots)
Control	2.0875	1.4000	3.4875	7.0425	9.8380	16.8805
C <sub>1</sub>	4.6745	3.6855	8.3600	11.5635	8.4170	19.9805
C <sub>2</sub>	10.4040	7.1320	17.5360	13.1115	9.0050	22.1165
C <sub>3</sub>	3.7045	3.5600	7.2645	19.3090	10.8550	30.1640
F <sub>1</sub>	3.2659	2.3565	5.6224	12.3845	9.8455	22.2300
F <sub>2</sub>	6.3765	4.8205	11.1970	11.7820	9.2520	21.0340
F <sub>3</sub>	2.3910	2.6520	5.0430	13.9940	13.1000	22.0940
M <sub>1</sub>	3.8980	3.1820	7.0800	8.0680	7.3095	15.3775
M <sub>2</sub>	6.8710	3.9095	10.7805	10.2030	8.8310	19.0340
M <sub>3</sub>	3.8310	2.0995	5.9305	13.5990	9.4975	23.0965
S <sub>1</sub>	4.0080	3.1625	7.6705	19.9480	8.8500	18.7980
S <sub>2</sub>	8.8935	5.3495	14.2430	12.1775	7.7330	19.9105
S <sub>3</sub>	4.3640	1.8630	6.2270	15.5640	11.2450	26.8090
'F' value of the treatments	558.5***	379.7***	1298.0***	614.0***	37.1***	273.3***
'F' value of the blocks	0.215	.015	0.276	0.875	0.197	.024
C.D. at the 5 percent level	0.2998	0.2324	0.3159	0.3680	0.5373	0.6800

\*\*\* Significant at the 0.1% level.

TABLE 7—UPTAKE OF POTASSIUM BY RICE PLANTS, MG.  
(Each Figure Represents an Average of Two Replicates)

Treatments	I.A.R.I. Soil		Total Uptake (Tops + Roots)	Sindri Soil		Total Uptake (Tops + Roots)
	Rice Tops	Rice Roots		Rice Tops	Rice Roots	
Control	6.8735	1.9280	8.8015	28.8740	27.5660	56.4400
C <sub>1</sub>	15.5810	5.4485	21.0295	36.2860	31.7415	68.0275
C <sub>2</sub>	29.3625	13.0505	42.4130	38.4305	36.4700	74.9005
C <sub>3</sub>	9.9645	3.8935	13.8580	50.9060	37.9920	88.8980
F <sub>1</sub>	13.5935	4.9415	18.5350	36.3545	29.1970	65.5515
F <sub>2</sub>	25.5060	9.6410	35.1470	35.5860	32.7370	68.3230
F <sub>3</sub>	7.8095	5.2155	13.0250	55.4395	34.7845	90.2240
M <sub>1</sub>	12.4740	5.5500	18.0240	34.9330	26.2675	61.2005
M <sub>2</sub>	19.4185	6.6160	26.0345	39.9615	30.4230	70.3845
M <sub>3</sub>	12.6430	4.2000	16.8430	51.4670	30.3920	81.8590
S <sub>1</sub>	14.7000	6.3970	21.0970	43.9365	30.0755	74.0120
S <sub>2</sub>	25.7730	10.5720	36.3450	49.1795	33.6205	82.8000
S <sub>3</sub>	13.5450	4.1400	17.6850	61.0595	49.7320	110.7915
'F' value of the treatments	541.07***	435.38***	1150.65***	359.32***	77.29***	273.14***
'F' value of the blocks	0.469	.011	0.428	1.271	0.286	.053
C.D. at the 5 per cent level	0.8729	0.4228	0.8487	1.4450	1.9618	2.5210

\*\*\* Significant at the 0.1% level.

(b) Sindri Soil (Table 7)

S<sub>3</sub> C<sub>3</sub> C<sub>2</sub> F<sub>3</sub> S<sub>2</sub> F<sub>2</sub> C<sub>1</sub> M<sub>2</sub> M<sub>3</sub> S<sub>1</sub> F<sub>1</sub> Control M<sub>1</sub>

Total Potassium (K) Uptake of the Whole R Plants  
(Tops + Roots)

(a) I.A.R.I. Soil (Table 7)

C<sub>2</sub> S<sub>2</sub> F<sub>2</sub> M<sub>2</sub> S<sub>1</sub> C<sub>1</sub> F<sub>1</sub> M<sub>1</sub> S<sub>3</sub> M<sub>3</sub> C<sub>3</sub> F<sub>3</sub> Control

(b) Sindri Soil (Table 7)

S<sub>3</sub> F<sub>3</sub> C<sub>3</sub> S<sub>2</sub> M<sub>3</sub> C<sub>2</sub> S<sub>1</sub> M<sub>2</sub> F<sub>2</sub> C<sub>1</sub> F<sub>1</sub> M<sub>1</sub> Control

Higher quantities of potassium were taken up by the multiphosphate treated plants in the I.A.R.I. soil, whereas in the case of Sindri soil superphosphate treated plants took more potassium than the other fertilizer treatment.

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# Energy Field of the Universe and Atom\*

By

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A new theory has been proposed on the constitution of the universe, which, as a single unified concept, appears to be capable of correlating and explaining the outstanding problems of science covering the following: universe of finite concept; significance of fundamental forces; gravitational and inertial motions, attraction and repulsion; significance of matter and energy; gravitational fields of the universe—atoms and their magnitudes; correlation of gravitational and magnetic fields and electromagnetic induction; significance of static and dynamic equilibrium; synthesis, disintegration and annihilation of matter; formation of material entity and chemical compounds; atomic and nuclear structural configurations, field energy, energy entities, charged particles and cosmic rays; corpuscular and undulatory nature of energy transmission—energy emission in the form of quantas; significance of the temperature and the absolute zero; kinetic and thermodynamic equilibrium. This theory is capable of explaining phenomena such as universe appearing expanding, planetary systems and the constancy of observed velocity of radiation, etc.

A finite spherical configuration of the universe of established radial gradients of potentials of matter, energy, space and time has been developed. The nature of the gradients and the modes of variation of the magnitudes of space, time, matter and energy in the field ensure the universe not only to remain in equilibrium as an entity, but also permit it only to manifest itself as a spherical stationary wave of varying potentials of matter, energy, space and time, with individual concentric spherical equipotential surface waves of varying magnitudes of these dimensions between maximum (characteristic for each surface) limits in opposite phases for each wave.

By applying a method of dimensional analysis, variations in the magnitudes of space, time, matter and energy with respect to one another and also with different types of energy fields have been worked out. Following the same the significance of fundamental forces of gravitation and gravitational equilibrium, significance of acceleration/retardation, gravitational and inertial motions, significance of matter and energy entities, mechanism and causes of attraction and repulsion of energy entities and charged particles have been deduced.

The constitution of the universal field and the modes of variation of the magnitudes of space, time, matter and energy therein lead to the manifestation of the universe as an irreversible phenomenon. The magnitude

of the universe depends on the degree of irreversibility prevailing within. It has been deduced that the radius (R) of the energy field of the universe can be represented by

$$R = S(1 + v^2),$$

in which S is a parameter determining the position in the field at which the overall equilibrium is established and v the magnitude of the ratio of space and time at equilibrium. Similarly, the radius (R') of an atomic field is indicated by  $R' = S(1 + 1/v^2)$ , the symbols S and v retaining the same significance.

It has been deduced that with infinitely high degree of irreversibility, the magnitude of the universe would be infinitely large with the magnitudes of total energy and ratio of space and time also infinitely high. If there would be perfect reversibility, the magnitude would be nil, having no content of matter or energy within. The universe with constant irreversibility maintains constant matter and energy content, and also space/time, matter and energy potential gradients.

The present postulates, employing associated dimensions of Gravitation, Stefan's and Gas constants, define temperature in terms of energy and space/time potentials, and lead to the conclusion that at absolute zero energy and space/time potentials would be nil.

In the light of the present postulates it has been explained why the universe to our perception would appear as an association of matter and energy entities in the form of a plane surface infinitum and the pheno-

\* This is a synopsis of a detailed dissertation by the author on the subject which is appearing separately.

menon of the universe as expanding. It also explains that if we were blind to light and sensitive to darkness, the universe could appear as contracting. It explains why emission of energy must take place in the form of discrete intermittent quanta, and, why the velocity of radiation would appear to us as constant. In the universal context, constant velocity of radiation can only be possible along a spherical equipotential path in the energy field; while radial emission along straight course involves variable velocity and energy potential gradient. Further, a radiation propagating through different energy fields of varying gradients of potentials of energy, space and time, should emerge with changed frequency, direction, velocity and wave length.

The mechanism of energy transmission in the energy fields, the constitution of positive and negative ions, atoms, and positively and negatively charged and neutral particles have been explained.

Application of the configuration of the energy field gives the distribution of energy units in the energy field of the universe in its kinetic as well as in the potential fields. The distribution in the potential field conforms to the equilibrium distribution of electrons in the atomic configuration of inert gases. It is suggested that the mode of distribution in the kinetic field should conform to the configuration and constitution of the nucleus of the elementary atom.

The present concept has been employed for a satisfactory explanation of formation of energy units, synthesis of elementary matter, formation of nucleus and atomic configuration, disintegration of elementary matter and formation of charged particles, certain properties of cosmic rays, transformation and annihilation of matter completely into energy, etc.

The development of polarity of energy during energy flow in the gravitational field and the consequent induced polarity of energy at equipotential surfaces have been explained. The polarised variation of magnitudes of space and time have been described. It has been shown that any change which may occur at any position in universe must have repercussions at all positions throughout.

The mechanism of establishment of dynamic and static equilibrium has been explained in the context of polarised variation of magnitudes of space and time. In the same context the mechanism of formation of stationary waves and the progressive waves has been reviewed.

It has been shown that the configuration of the energy field of the universe with the potential gradients of energy, space and time is exactly equivalent to field configuration of a magnetic dipole. Transformation of an equipotential surface wave with its usual polarised variations of the potentials of energy, space and time into field of a magnet has also been worked out, retaining the characteristic variation of space and time at the equipotential surface. Similarly, the generation of induced polarity due to an energy flow in the energy field has also been translated into a configuration of induced electromagnetic field.

The theory can explain the mechanism and the causes of formation of lump of material entity as continuous matter, such as metals, and formation of crystals, etc.

The mechanism of formation of chemical compounds with respect to covalent and ionic linkages can also be explained. The relative difference in magnitudes of radius of atom with those of positive and negative ions has been explained with the help of the relationship mentioned before for an atomic field.

# Automatic Gas Analysers

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In recent years, a new kind of process analysers has been introduced in the chemical and other industries. By applying the fundamental physical properties of the components to be analysed, these have replaced the conventional equipment comprising glass apparatuses and chemical reagents with electrical and electronic gadgets. The principles of the working of these analysers have been discussed here.

In all modern processes, the attempt has continued to provide such effective methods of measurement and control as can dispense with the human element and give optimum efficiencies and uniformity of products at lower costs in less time. The measurement is not limited to the well-known parameters like flow, level, temperature, pressure and pH only, but has advanced to the continuous and accurate analysis of the process streams. The importance of automatic gas analysis can well be realised from its wide application in all industries. Many of the laboratories and industrial enterprises are constantly trying to replace the existing methods of chemical analysis by automatic continuous methods.

Although the initial cost of the process analysers is high, yet it is justified for the various benefits derived from such measurements, viz. in the form of uniform product quality, check on the wastage at various stages of the process and the safety of the equipment and personnel.

The basic function of an analyser is to determine a particular component in a mixture of gases. Therefore, the actual parameter which is to be measured by an instrument must be specific for the desired component in any given mixture. Considering, for example, the case of ammonia synthesis gas mixture in which it is essential to keep the concentration of oxygen and carbon monoxide very low for the efficient production of ammonia and for avoiding any damage to the catalyst. For analysis of oxygen in this range, the electrochemical method of oxygen determination is specifically made use of, whereas for carbon monoxide the infrared absorption technique is applied.

Similarly, for determining the impurity of oxygen in nitrogen obtained from the Linde air-fractionating

unit, the paramagnetic property of oxygen is utilized. Further, in order to determine the purity of carbon dioxide of water scrubbing section, thermal conductivity property is utilized.

## 1. Thermal Conductivity Analysis

The working of thermal conductivity analysers is based on the well-known principle that different gases have different heat conducting capacities. This fundamental principle with the help of a Wheatstone bridge provides a means for the determination of gases like carbon dioxide, ammonia, sulphur dioxide and hydrogen, etc. A comparison of thermal conductivities for some of the gases is illustrated in Fig. 1.

The instrument consists of four cells A B C & D (Fig. 2). In each cell, a platinum wire of known resistance is connected, and the four wires of identical resistances thus connected form four arms of the Wheatstone bridge. The measuring gas, regulated at a constant flow, passes through the measuring cells, A and B, placed opposite, whereas the reference gas flows through C and D or, for convenience, it can be sealed in these cells.

The bridge current is supplied from a dry cell or a constant voltage transformer which heats all the wires equally. When the sample gas passes through the cells A & B, it carries away heat depending upon its thermal conductivity from the platinum wires, thus changing the resistance. Similarly, the resistance of wires C & D is also altered depending upon the thermal conductivity of the reference gas. This makes the bridge unbalanced and produces a voltage, proportional to the gas concentration across the diagonally opposite points L & M. This voltage can be fed to a suitable electrical indi-

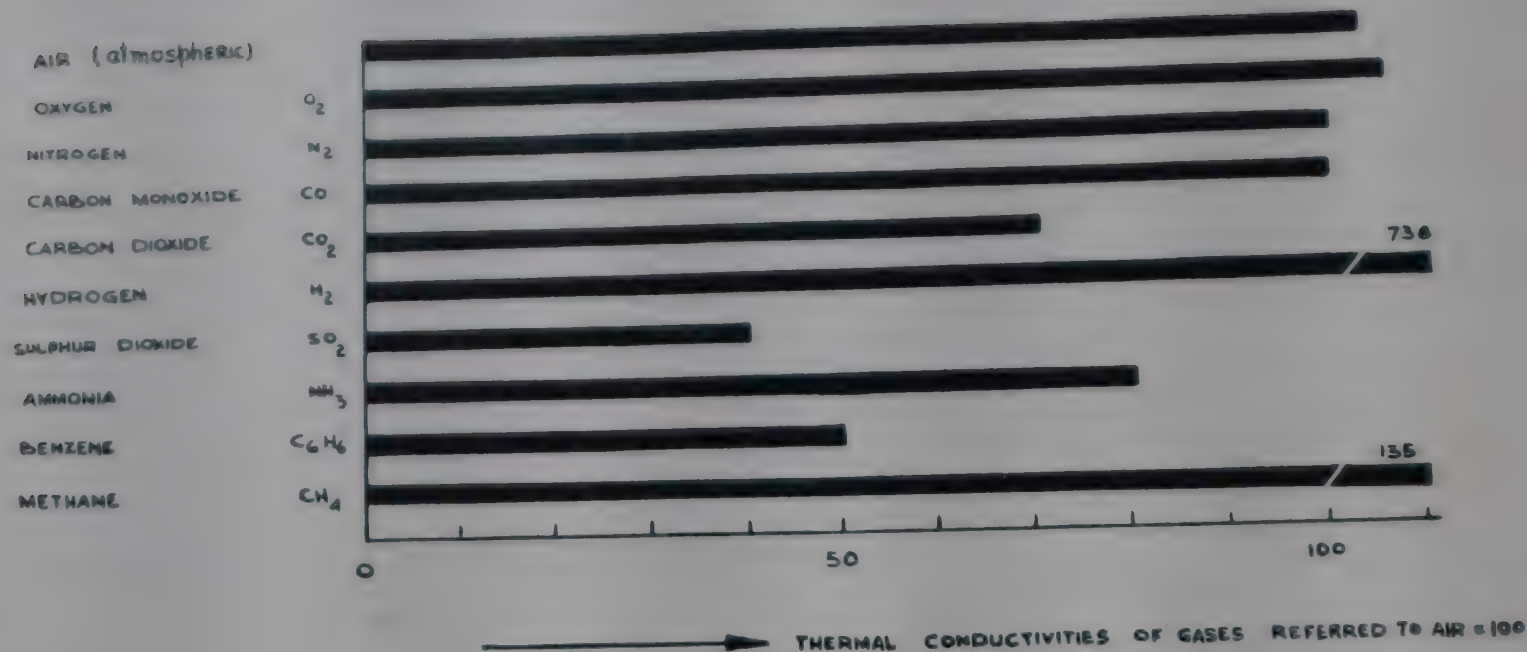


Fig. 1. Thermal Conductivities of Various Gases at 100°C.

cating, recording or controlling instrument, which in turn is calibrated in terms of gas concentration.

The zero of the instrument can easily be checked by passing the same gas through all the four cells. In this condition, all the four elements dissipate heat equally, and their resistances, remaining unaltered, keep the bridge in a balanced condition.

In the application of this method, it is essential that the thermal conductivity of the measuring component in a binary mixture must vary distinctly from the other component. Some of the important applications of thermal conductivity analysis are given below (Table 1).

TABLE 1—APPLICATION OF THERMAL CONDUCTIVITY ANALYSIS

Range, %	For Analysis of Gaseous Components in
0 - 100 CO <sub>2</sub> (all ranges)	Flue gases from boilers and industrial furnaces.
95 - 100 CO <sub>2</sub>	Carbon Dioxide Water Scrubbers
0 - 30 H <sub>2</sub> 0 - 100 H <sub>2</sub>	Producer gas. Hydrogen from Water electrolysis. Raw Gas for Ammonia Synthesis
0 - 15 NH <sub>3</sub> 0 - 25 NH <sub>3</sub>	Ammonia Synthesis
0 - 10 SO <sub>2</sub> 0 - 20 SO <sub>2</sub>	Sulphuric Acid Plants,
0 - 1 H <sub>2</sub> in Oxygen 0 - 1 Oxygen in Hydrogen	Electrolysis. Atmospheric Control Plants.
0 - 5 HD in H <sub>2</sub> 80 - 100 HD in H <sub>2</sub>	Manufacture of Heavy Water

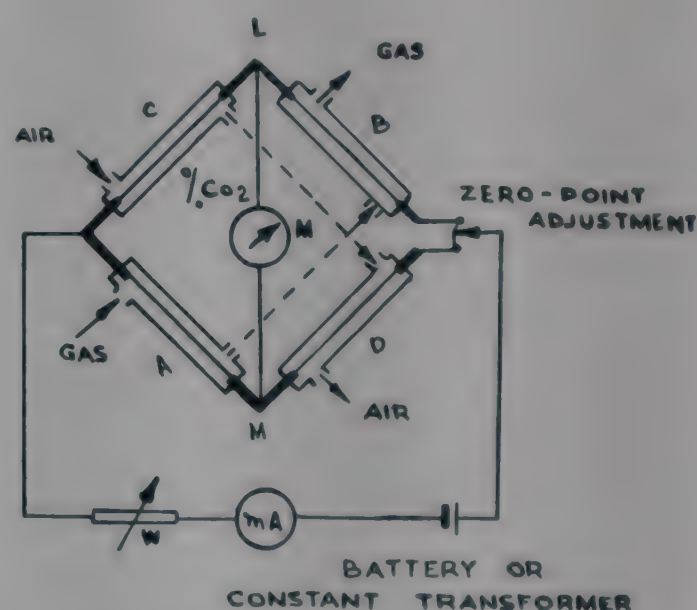


Fig. 2. Heat Conductivity Instrument.

## 2. Oxygen Analysis

Oxygen plays an important role in many of the chemical reactions, viz. combustion of fuels, biological and metabolic processes, etc. On account of widespread applications, special efforts have been made to find out some of the physical properties of oxygen molecules to use them for automatic oxygen analysis. This pursuit has led to the development of magnetic oxygen analysers.

(i) *Paramagnetic Oxygen Analyser*. It has been observed that most of the gases when subjected to a non-uniform magnetic field, tend to move from stronger to weaker parts. Such gases are termed as diamagnetic gases. The notable exceptions to this common behaviour are oxygen and nitric oxide gases which have the opposite property i.e. of moving towards the strongest parts of the magnetic field. These are known as paramagnetic

gases. The magnetic properties of a substance are measured in terms of susceptibility which is defined as:

$$K = \frac{I}{H}$$

where  $K$  = Volume Susceptibility

$I$  = Magnetic Intensity

$H$  = Intensity of Magnetic Field.

Fig. 3 gives a comparative idea of volume susceptibility of various gases. It is evident that out of all the gases, oxygen has very strong paramagnetic properties. This property has been utilised in the development of oxygen analysers for determination of oxygen down to 0.1 per cent by volume.

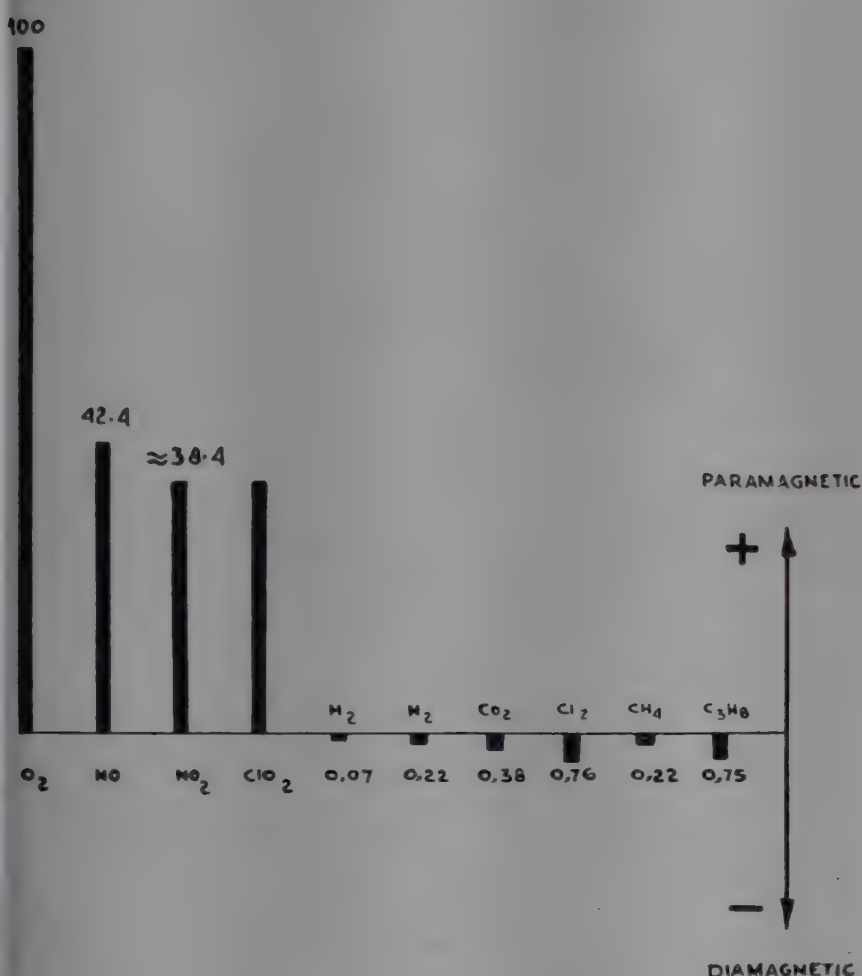


Fig. 3. Relative Magnetic Values of Various Technical Gases.

The present method, which was developed by Dr. Lehrer of Germany, is based upon the magnetic wind principle. The measuring gas drawn into the ring chamber passes through the annulus and leaves the chamber at the opposite end (Fig. 4). The chamber contains a horizontal diametrically situated thin-walled glass tube (G) which is fitted with two adjacent identical platinum windings. These windings form the two arms of a Wheatstone bridge. The left hand part of the tube is subjected to a strong magnetic field by placing it between the poles of a powerful permanent magnet. When

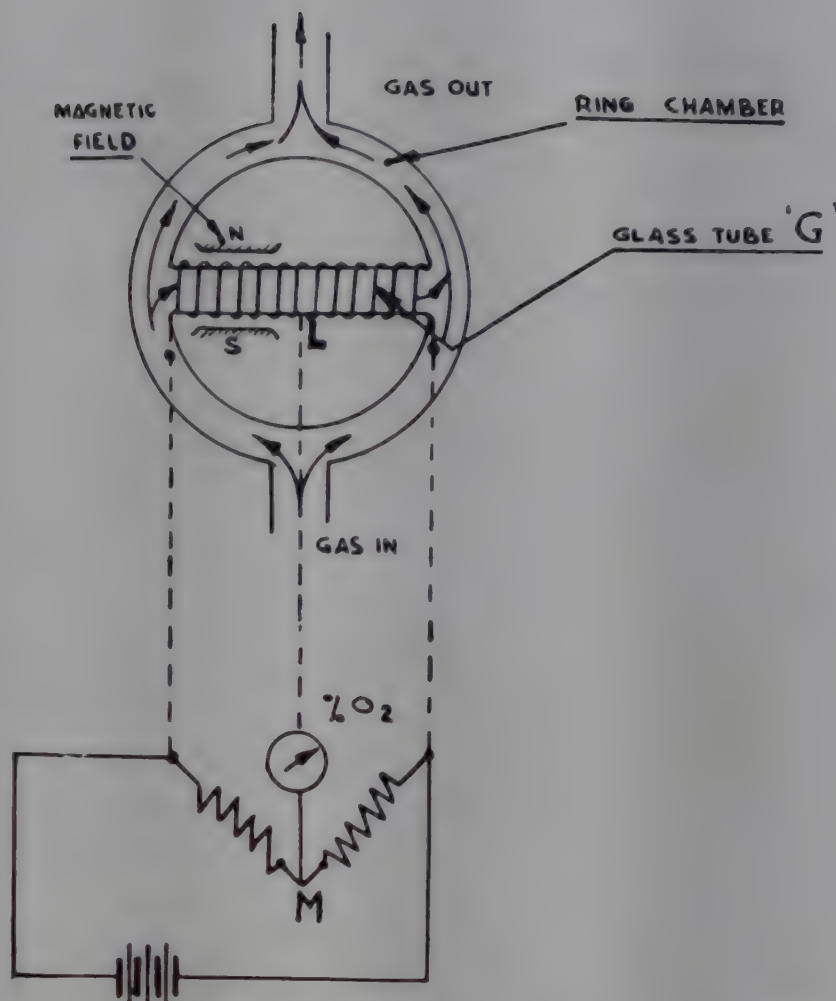


Fig. 4. Lehrer's Apparatus for the Measurement of Oxygen.

a gas containing oxygen is introduced into the ring chamber, it is drawn into the magnetic field and enters the tube which is heated by the platinum windings. By passing through the tube, the gas becomes heated, and its susceptibility is reduced according to the following relationship:

$$K = \frac{C}{T^2}$$

Where  $K$  = Volume Susceptibility

$C$  = Constant

$T$  = Temperature

With the decrease in susceptibility, the hot gas is displaced from the magnetic field by the fresh gas which is attracted more into the magnetic field because of its higher susceptibility. With this action, gas flows continuously from left to right of the horizontal tube, and this phenomenon is referred to as "Magnetic Wind". The velocity of magnetic wind depends upon the oxygen concentration.

Now, the flow of gas through the tube cools the left-hand winding as the heat is taken away by gas. This hot gas while passing through the right-hand winding, gives a part of its heat to the winding which in turn is heated up. Thus the electrical resistance of the left-

hand winding is decreased as compared to the right-hand winding and the bridge is unbalanced. The unbalanced voltage between the diagonally opposite points L & M is measured by a suitable instrument and is proportional to the oxygen concentration.

The measuring instrument can be an indicator, a recorder or a controller, and is calibrated in terms of percentage of oxygen. The zero of the instrument can be checked conveniently by passing pure nitrogen through it, the final calibration being done by passing a sample of known percentage of oxygen. Some of the applications of the paramagnetic oxygen analyser are given below (Table 2).

TABLE 2—APPLICATION OF PARAMAGNETIC OXYGEN ANALYSER

Range, % by Vol.	For Analysis in Gases
95 - 100 Oxygen 0 - 1	Product Oxygen from Air Liquefaction plants.
0 - 10 Oxygen	Flue gases from boilers and furnaces of all types.

(ii) *Electro-Chemical Method*. This method has been used successfully in determining traces of oxygen. It consists of a galvanic cell with a pair of lead and silver electrodes immersed in the electrolyte (Fig. 5). The

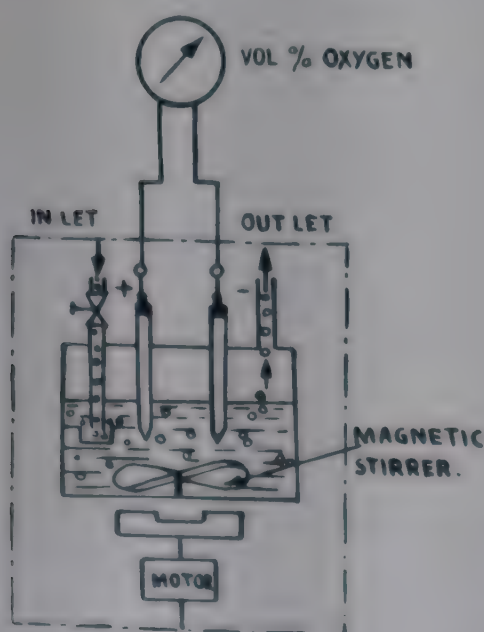


Fig. 5. Trace Oxygen Measurement by Electrochemical Method.

sample gas is passed through the electrolyte, which is kept under agitation to ensure uniform distribution of the gas in the electrolyte. According to Henry's law, a definite relationship exists between the oxygen dissolved in the electrolyte and the oxygen partial pressure of the adjoining gas phase. Oxygen reacts with hydrogen ions and decreases the polarization on the lead cathode and

thus produces an electromotive force and a current which are definite functions of the partial pressure of oxygen or the oxygen concentration. The electric current of the order of Micro-ampere is measured with a suitable instrument, and it is calibrated in terms of parts per million of oxygen. The instrument has ranges like: 0-10, 0-100 and 0-1000 ppm.

(iii) *Dissolved Oxygen Analyser*: This instrument is widely used in determining minute quantities of dissolved oxygen in boiler feed water (Fig. 6). It is based

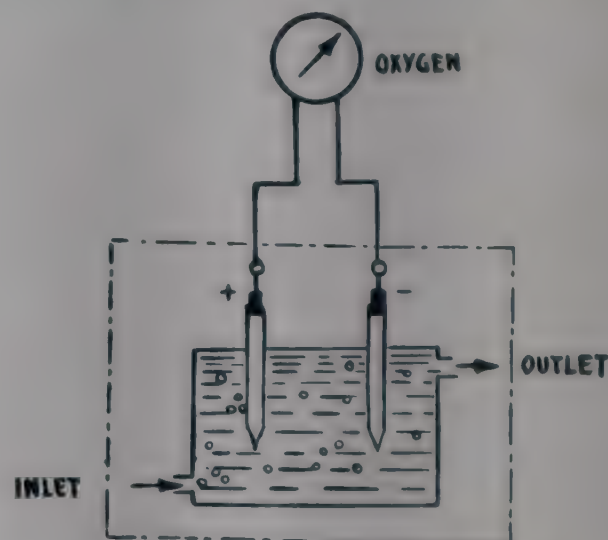


Fig. 6. Dissolved Oxygen Measurement by Electrochemical Method.

upon the principle of galvanic cell as mentioned earlier. In this case, instead of a special electrolyte, the water itself acts as an electrolyte in which the two electrodes are immersed. The electric current produced across the electrodes is in direct proportion to the dissolved oxygen in water. The standard range for such applications is 0 to 0.2 ppm. oxygen.

### 3. Infrared Analysis

As the name signifies, the analysis is based upon the fact that all gases except the rare and the diatomic ones, like oxygen, nitrogen and hydrogen, absorb infrared radiations. The infrared absorption spectrum of various gases is shown in Fig. 7.

If an infrared ray of wave length  $\lambda$  and intensity  $I_0$  passes through a gas over a distance  $D$  and has a molecular concentration  $C$ , the intensity  $I$  of the ray after absorption is expressed by

$$I = I_0 e^{-\epsilon(\lambda) \cdot C \cdot D}$$

which is known as Lambert—Beer law.

It is clear from this relation that the absorption increases with the increased concentration of gas compo-

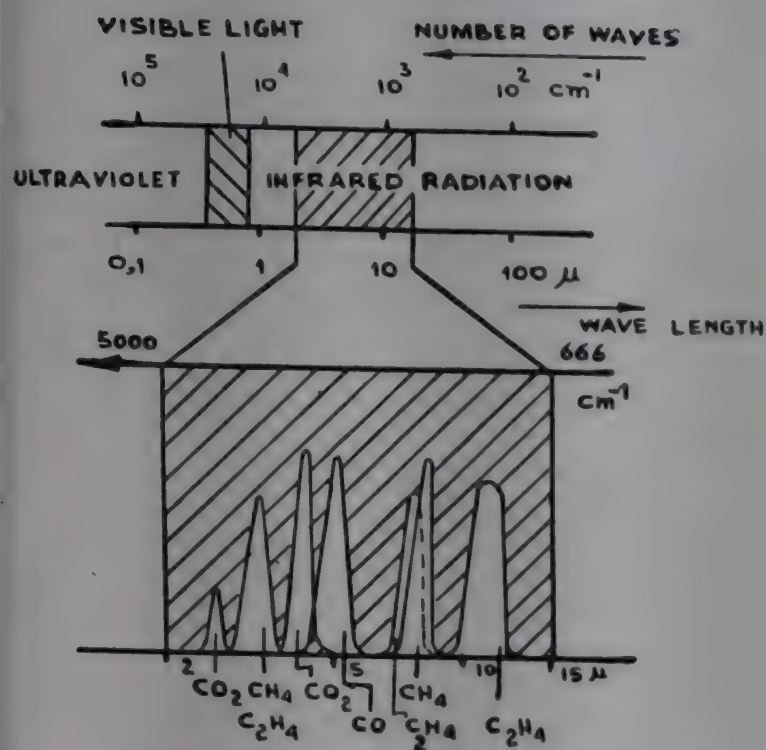


Fig. 7. Diagram of Electromagnet Radiation Spectrum

ent and the distance through which infrared radiations pass. The decrease in radiation as a result of absorption in gases can be measured by bolometer or thermopile. As these methods need an elaborate set-up for

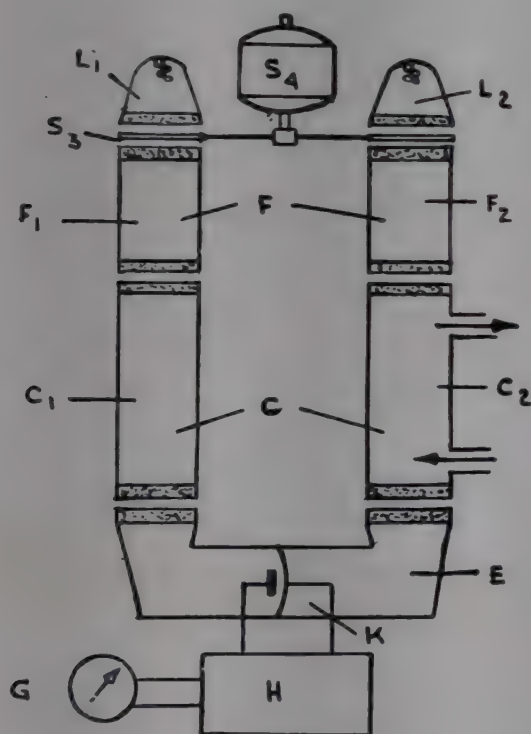


Fig. 8. Diagram of the Infrared Analyzer Operating Principle.

- $L_1, L_2$ —Radiator with Parabolic Mirrors.
- $S_3$ —Rotating Vane.
- $S_4$ —Motor.
- $F$ —Filter Cell.
- $F_1/F_2$ —Filter Chamber
- $C$ —Measuring Cell.
- $C_1$ —Reference Chamber.
- $C_2$ —Measuring Chamber
- $E$ —Receiver.
- $K$ —Diaphragm Capacitor.
- $H$ —Amplifier.
- $G$ —Electrical Indicator or Recorder.

accurate measurement, they have now been replaced by a more versatile and rugged equipment (Fig. 8). The infrared radiations are emitted by two similar chrome-nickel coils,  $L_1$  &  $L_2$ , which are heated electrically. These coils are placed at the focal points of the parabolic mirrors. The collimated rays pass on one side through the measuring chamber  $C_2$  through which the sample gas flows and on the other side through the reference chamber  $C_1$  in which the reference gas, generally nitrogen, is sealed.

The rotating vane  $S_3$  consists of two sector discs which are driven by a synchronous motor (Fig. 9). This interrupts the radiations simultaneously in both the beams, and then admits them in the respective chambers at frequency in the range of 1-20 cps.

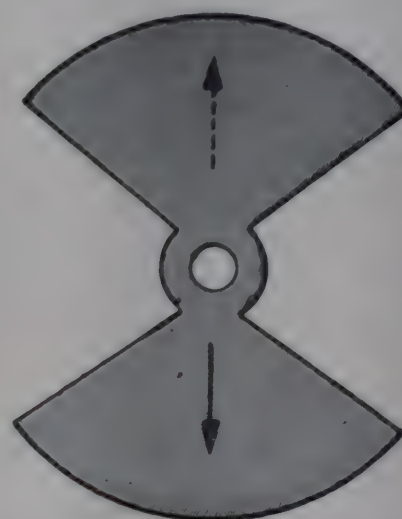


Fig. 9. Rotating Vane.

After passing through the measuring and reference chambers, the radiations are received in the receiver  $E$ . It consists of two compartments of equal volume separated in the middle by a metal diaphragm. Both the compartments are filled with the mixture of gas containing the measuring component of the sample gas and argon. This is done so that the instrument is responsive for a given gas without spectral diffraction. This means that the receiver shall be absorbing the radiation only in the absorption band of gas under measurement.

For example if carbon dioxide is to be analysed in a gas mixture, it is filled along with argon in the receiver. When the gas sample containing carbon dioxide flows through the measuring chamber, the specific bands corresponding to carbon dioxide shall be absorbed from the infrared radiations. Thus, the right-hand side of the receiver shall receive the specific bands corresponding to carbon dioxide which have been weakened. On the other side, the radiations passing through the reference

chamber containing nitrogen, shall not at all be absorbed. Accordingly, the unabsorbed infrared radiations enter the left-hand compartment of the receiver. The carbon dioxide bands shall be absorbed by the filled gas, and with the absorption of this energy, the gas gets heated up more than the gas in the right-hand compartment. This gives rise to difference in temperature across the compartments, and the concentration of gas component is proportional to this temperature difference which is of a very small magnitude.

In order to measure this temperature difference, a diaphragm condenser K is placed between the two compartments. Due to the rotating vane and the periodic interruptions of the infrared rays, the temperature difference in the receiver changes at a constant frequency. These temperature variations are interpreted as pressure. fluctuations producing constant vibrations in the diaphragm. As this diaphragm serves as one plate of a parallel plate condenser and due to diaphragm vibrations, the capacity of the condenser shall change constantly. This change in capacitance is converted to an A. C. voltage and amplified by an electronic amplifier. The output of the amplifier, after rectification, is fed to a suitable measuring instrument calibrated in terms of the percentage of gas under analysis.

In addition to the measuring component, if some other gas having absorption band in the same region is present in the mixture, then there will be a change in deflection due to overlapping of the bands. This condition will cause false readings. In order to eliminate this cross sensitivity, two filter chambers  $F_1$  &  $F_2$ , which are filled with the gas component causing this interference, are placed in the path of the infrared radiations.

Some of the applications of infrared analysis are given below (Table 3).

TABLE 3—APPLICATIONS OF INFRARED ANALYSIS

<i>Measuring Component</i>	<i>Lowest measuring range</i>	<i>Maximum range, % by vol</i>
$\text{CO}_2$ , $\text{N}_2\text{O}$	0 - 50 ppm	
CO	0 - 100 ppm	
$\text{CH}_4$ , $\text{C}_n\text{H}_{n+2}$ , $\text{C}_2\text{H}_2$	0 - 200 ppm	0 - 100
$\text{NH}_3$ , HCl	0 - 1000 ppm	
$\text{H}_2\text{O}$ , $\text{CH}_3\text{OH}$ , Petrol	0 - 1, Og/m <sup>3</sup>	

#### Acknowledgement

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## Pressure Reducing Valves

By

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It is generally more economic to lead high pressure steam to consuming plants and get the pressure reduced there according to plant requirements or limitations. Pressure reducing valves are used for such reduction of pressure within predetermined specified limits.

Pressure reducing valves are used for reducing pressure automatically in a supply line and controlling it within reasonable limits of a predetermined value irrespective of the flow rate. Being self-contained items, they need no external source of power for their operation and they perform no recording or indicating function. These can be used for condensible (steam), non-

condensible (dry gas) or incompressible fluids. The last type has, however, not been included in this article.

#### Principle

A pressure reducing valve consists essentially of a direct-seating valve, which is held normally fully open by a spring and is closed by a suitable diaphragm or

piston to which the pressure is applied in the reduced or downstream side. The diaphragm area and the spring characteristics are so related that the system is in balance at the desired reduced pressure setting, and this is varied normally within limits by adjusting the spring. Thus, increasing the spring load will normally increase the reduced pressure and vice versa.

## Types

There are in general the following three types of pressure reducing valves: (i) simple reducing, (ii) relay type, and (iii) direct acting balanced type.

(i) *Simple Reducing Valves*: This type has the following advantages: it is simple, cheap and fundamentally reliable; it provides a very tight shut-off when there is no demand on downstream side.

As regards its drawbacks, the following are significant: (a) its accuracy of control is not very precise; the downstream pressure falling progressively as the flow increases, from a maximum limit at zero or a very small flow. This characteristic is often called "droop"; (b) the downstream pressure is affected to some extent by fluctuations in the upstream pressure, which is sometimes referred to as "sympathetic variation"; (c) it is not suitable for very high pressure or temperature.

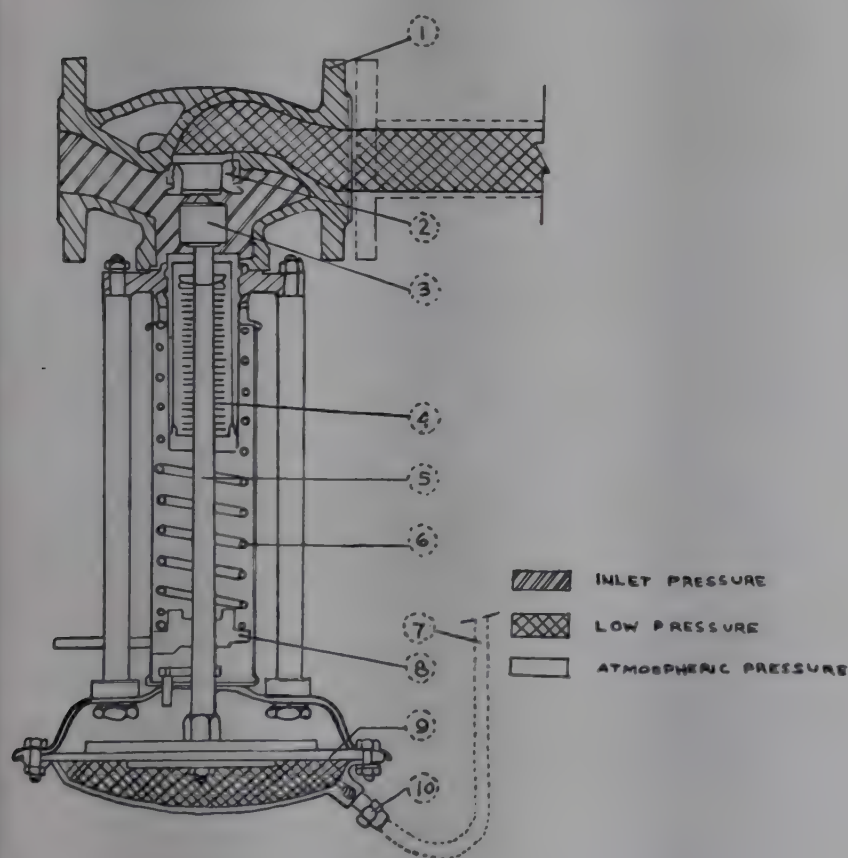


Fig. 1. Reducing Valve

- |                             |                             |
|-----------------------------|-----------------------------|
| 1. Valve Body.              | 6. Pressure Spring.         |
| 2. Valve Seat.              | 7. Impulse Pipe.            |
| 3. Valve Cone.              | 8. Low Pressure Adjustment. |
| 4. Balancing Metal Bellows. | 9. Operating Diaphragm.     |
| 5. Spindle.                 | 10. Impulse Pipe Connexion. |

However, there are many applications for this simple type of valve where the advantages outweigh the disadvantages, e.g. if a vessel filled with a liquid requires to be emptied by means of a dip pipe and applied air pressure. The vessel has a working pressure of 30 psig, and the air supply is available at 1000 psig. The pressure-volume regulations prohibit direct connexion of air at 1000 psig to a vessel of lower rating without a suitable safeguard against air-pressure. In this case such a simple reducing valve is ideal, since it is there to limit the maximum pressure rather than to provide a precise working pressure.

As regards its drawbacks, it has been found that there is an inverse flow/reduced pressure relationship in the simple single diaphragm valve. Since the equilibrium pressure on the diaphragm for any given flow will vary in direct proportion to the spring load for that position of the valve corresponding to the flow at that time, the latter will vary in relation to the spring rate. At first sight the lower the spring rate the better the control. By going to the extreme, say zero or very low, spring rate will give an unstable value, since there is a pressure drop across the valve head which may not be constant and the spring rate must always be greater than this for stability.

The second drawback is that a diaphragm will have a very limited travel if it is to have a reasonable life so that the lift of the valve may be limited. This makes its larger sizes less suitable.

(ii) *Relay Valve*: Where an accuracy of downstream pressure control over a wide range flow is essential, most of the makers supply, in one form or other, a relay type valve. Essentially, this type embodies its own servo-mechanism on the following principle: The main valve is single-seated held closed by a light spring, and separated from this mechanically is a diaphragm which is subject to the downstream pressure on one side and an adjustable spring in opposition on the other. The movement of the diaphragm actuates a small pilot valve having an arrangement such that with less than the desired pressure downstream, the spring deflects the diaphragm and causes the pilot valve to open. With the downstream pressure equal to the desired value, the force on the diaphragm is balanced against the spring and therefore the pilot valve closes.

When the downstream pressure is low, the pilot is open and live steam is admitted to a servo piston, meant to overcome the main valve spring and any out-of-balance steam pressure, so that the main valve opens and admits steam to the downstream system until the

setting pressure is reached. A small bleed before the piston allows the live steam to escape once the pilot valve is closed, and permits the main valve and the piston to return towards the closed position until an equilibrium is reached where the amount of steam passing the main valve is equal to the demand.

The advantages of this type of relay valves may be summarized as below: they are almost free from "droop", "sympathetic variation" and hysteresis; are suitable for very high pressures and temperatures; they have compact dimensions for large flow capacities.

The major drawbacks are: increased complexity leading to increased cost and maintenance; greater sensitivity to dirt.

The main reason for the technical superiority and improved performance of the relay valve lies in the diaphragm which operates a very small pilot valve with a small amplitude of movement in complete freedom from secondary effects. Thus a compact diaphragm, balanced against a low rate spring, can give good regulation with adequate servo power from live steam to operate the main valve and overcome hysteresis.

(iii) *Direct-Acting Balanced Valve*: The direct-acting valves give an improved control compared to the basic simple direct-acting ones. In this type, the principle of pressure balance by means of a diaphragm and an opposing spring is retained, so that it still suffers from some degree of 'droop'. The 'sympathetic' variation is corrected by having a second diaphragm arranged on the same spindle in such a way that it balances the pressure difference across the main valve and permits a lower rate spring for use. In this way, 'droop' is appreciably reduced.

### Selection of Valves

The main factors affecting the selection of the type of valve are in the following order of importance: (a) medium to be controlled—steam (condensing) or air; (b) pressure—initial and differential; (c) temperature, and in the case of condensible whether superheated or saturated; (d) degree of control required; and (e) the nature of flow—maximum, minimum and mean. The influence of the above factors on the choice can be summarised as below:

If the valve is needed for steam, there will be occasions when no steam being in use the valve will apparently have to be shut off tight to avoid pressure build-up. However, downstream of the valve condensation will continue representing a very small demand which a direct-acting valve can meet only by 'wire-drawing'

with a corresponding loss of life and heavy seat wear.

Most relay type valves are so designed that the pilot valve steam is ultimately bled into the downstream system, and this is usually adequate to make up condensation losses so that the main valve can remain seated tightly on 'dead-end' duty.

Again, because of the small movement needed from the diaphragm of a relay type valve, it is possible to select a suitable metal for this job with better expectation of life at elevated temperatures and pressures. With the possible exception of specially supported diaphragms, most direct-acting valves demand a diaphragm travel, which needs a rubber or a similar elastic material for its accommodation.

Some steam valves of the direct-acting, particularly the pressure-balanced, type are made with rubber diaphragms, such that these are at the temperature in conjunction with the exposed radiating surfaces. With superheated steam, it is imperative that metal diaphragm valves be used as there will be no condensate formation. This is a point which dictates the use of a relay valve. Valves used for steam, apart from being very simple and capable of pressure duties, should always be of the relay type and be fitted with appropriate alloy trim to withstand the working conditions.

While handling the non-condensibles, condensation problem however does not arise, and a tight shut-off is important. Valves with rubber diaphragms and possibly seats also are, therefore, a logical choice.

### Size of Valves

Mistakes in the choice of a valve are of consequence. If the valves which are installed are *too big*, for a large part of their life they are worked with small openings with resultant high velocity and causing erosion of the valve seat. It is better and more convenient to use a smaller size—even by two sizes—valve that the calculations warrant, if peak loads are infrequent. Some manufacturers provide reduced size intervals for a standard size, which means that in the event of a load increase or the valve not being large enough the interval trim can be replaced by a larger set without the cost of a new one.

### Installation

Most of the manufacturers provide instructions which should be followed accurately if satisfactory service is to be achieved. Some of the relevant and useful points may be emphasized as hereunder:

(a) there should be a suitable isolating valve upstream of the reducing valve;

(b) a strainer should always be fitted before a reducing valve to trap any pipe scale, which will cause damage particularly to new installations. Strainers should have adequate area to avoid undue pressure drop ahead of the reducing valve at maximum flow;

(c) adequate capacity should be provided in the downstream pipe work to give stable regulation; reducing valves will tend to give poor regulation, if they are followed immediately by a flow regulating valve;

(d) Over-pressure protection must also be provided in conformity with safety regulations. A safety valve capable of releasing maximum flow through the reducing valve kept wide open and without permitting more than 10 per cent rise above the designed reduced pres-

sure must be provided. Where the reducing valve is effecting a large pressure reduction to a low reduced pressure, the safety valve may have to be very large since the permissible rise in pressure may be very small. This point requires careful consideration since the over-size reducing valve may involve a very large and expensive safety valve installation;

(e) a pressure gauge must be provided downstream of the reducing valve for setting the valve accurately after installation;

(f) in steam installations, a steam trap must be provided between the reducing valve and the first downstream isolating valve; and

(g) for setting purposes, it is useful to have a small ( $4\frac{1}{4}$ " dia.) bleed valve just downstream of the reducing valve to bleed off accumulated pressure and to test the operation of the valve.

## Particle Size of Coating Agents

By

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The importance of proper control on the particle size of coating agents has been emphasized, as it ensures uniform coverage and adequate retention. Blaine's instrument has been found useful for this purpose, because it is simple and indicates conveniently the degree of fineness of the coating agents.

Coating of fertilizer granules with pulverised materials, such as limestone, soapstone, kieselguhr, tricalcium phosphate, etc., is one of the important and most prevalent methods employed to keep the fertilizer in a free-flowing condition. Effectiveness of these coating agents depends mainly on their ability to absorb 'available' moisture present in the form of saturated solution rendering it unavailable for the formation of intergranular bridges.

In order that these coating agents are fully effective, it is necessary that the granules are coated uniformly and the pulverized material remains adhered to the granules. Particle size of the coating agents is extremely important in this context. The coarser particles lead to un-uniform coverage and weak adhesion.

Normally, the specification given for coating agents is as follows: 80 or 100 per cent material should pass through 100 mesh (B.S.) sieve. In view of the close relationship between the particle size of the conditioning material and its anti-caking effect, a more rigid specification appears to be necessary. This is possible if the proportion of particles falling under sub-sieve ranges is also taken into account.

Need, therefore, was felt for a simple apparatus that would keep a check on the fineness of the material in a running plant. Blaine's apparatus with some modification has proved promising. This apparatus is simple and can be fabricated without difficulty. The principle involved is the measurement of the time for a set volume of air to flow through a packed bed of particles. Similar instruments are in use in the industry, especially for cement. The sophisticated ones, based on similar principle, are also available

The relationship between time of flow and specific surface of particles is given by Kozeny-Carmen equation,

$$S = \frac{K e^{\frac{3}{2}} T^{\frac{1}{2}}}{\rho \mu^{\frac{1}{2}} (1-e)} \quad (i)$$

Where  $S$  = Specific surface, sq.cm. per g.

$K$  = Constant

$T$  = time for the air to pass through the sample bed, secs.

$\rho$  = powder density, g./c.c.

$\eta$  = viscosity of air, poises

$e$  = fractional void space =  $1 - W/\rho V_c$

Where  $W$  = weight of the powder sample.

$V_c$  = Volume of cylinder.

The equation (i) can be put in the form,

$$T = \frac{\rho^2 \eta}{K_1} \frac{S^2 (1-e)^2}{e^3}$$

For a given instrument and a given material,

$$T = K_2 \frac{S^2 (1-e)^2}{e^3}$$

The above equation implies that time of flow is proportional to the square of specific surface, which is a function of particle size. Thus the specification of coating agents can be laid down in terms of the time of flow in seconds, which would ensure the optimum overall distribution of its particle size.

This is often difficult to achieve as it requires elimination of the design factors by standardizing the size of the sample cylinder, manometer and manometer fluid.

The fluid-draining properties are influenced signi-

significantly by even slight impurities present in the manometer fluid or dirt sticking to the walls of the manometer. The error is noticeable even when using the same sample on different instruments, which have been calibrated against the same standard. This can be overcome by using a number of standard samples which will cover effectively the full range of specific surface to be measured.

In view of these complications, the solution lies in keeping the standard sample of the coating agent of desired particle size distribution in the various chemical control laboratories of the producing units, and in

getting its time of flow determined and compared with that of the conditioning material being added into the coating drum.

This instrument along with our caking apparatus<sup>1</sup>, already in use in the units of F.C.I., would greatly supplement our efforts to produce a better quality non-caking fertilizer.

#### REFERENCE

1. Varma, S., Jayaraman, R. & Chakravorty, K. R., *J. sci. & industr. Res.*, 18B (1959), 118-122.

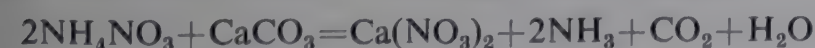
## A Method for Direct Estimation of Calcium Nitrate in Calcium Ammonium Nitrate Fertilizer

By

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Ammoniacal methyl alcohol—97 ml. methyl alcohol: 3 ml. of aqua ammonia containing 0.134 g.  $\text{NH}_3/\text{ml.}$ —has been found to extract calcium nitrate from calcium ammonium nitrate fertilizer leaving behind calcium carbonate. Calcium nitrate in the fertilizer is estimated by distilling off methyl alcohol from the extract, dissolving the residue in water and finally analysing the solution for its calcium content by the standard volumetric method using potassium permanganate

Calcium ammonium nitrate or Nitro-limestone fertilizer is a mixture of ammonium nitrate and calcium carbonate. The proportions of the two components are so adjusted that the total nitrogen content of the final product is about 20.5 per cent. In the usual process of manufacture of this fertilizer, powdered limestone is added to ammonium nitrate melt containing about 6-10 per cent water and the mixture is granulated and dried. During this process of mixing and drying, a reaction to some extent takes place between ammonium nitrate and calcium carbonate according to the equation:



A portion of nitrogen is thereby lost as ammonia and some calcium nitrate is formed simultaneously. A

knowledge of the calcium nitrate content of the product, therefore, gives an idea of the loss of nitrogen on this account. The estimation of calcium nitrate in the fertilizer is desirable for this reason, and also because of the necessity of controlling the calcium nitrate in the product to a low value to reduce its hygroscopicity and caking tendency.

Calcium nitrate in nitro-limestone is usually estimated indirectly from the values of ammoniacal and nitrate-nitrogen in the fertilizer. Since in ammonium nitrate the amounts of ammoniacal and nitrate-nitrogen are equal, any excess of the latter over the former in nitro-limestone is taken to be due to the presence of calcium nitrate.

In the present investigation, a method has been evolved for direct estimation of calcium nitrate in the fertilizer. The method is based upon the fact that calcium carbonate in nitro-limestone is practically insoluble in methyl alcohol containing a little ammonia whereas the solubility of calcium nitrate in the same solvent is quite appreciable. The following is the procedure, according to the new method, for the estimation of calcium nitrate in the calcium ammonium nitrate fertilizer.

The fertilizer granules (5-10 g.) are weighed out into a 500 ml. Erlenmeyer flask, and ammoniacal methyl alcohol (50 ml.) is added to extract the calcium nitrate. For preparing this liquid, 3 ml. of aqua ammonia (containing 13.4 g./100 ml. of ammonia) is added to every 97 ml. of methyl alcohol. The contents of the flask are stirred magnetically at 20°C for 20 min. By this time the granules fall into powder. The mass is filtered through a Whatman No. 42 filter paper into a 500 ml. wide mouth Erlenmeyer flask. The residue from the original flask is transferred to the filter paper and washed with ammoniacal methyl alcohol (4×25 ml.) and the washings added to the original filtrate. The methyl alcohol from the Erlenmeyer flask is removed by distillation. The solid residue in the Erlenmeyer flask is dissolved in water, and calcium is estimated in the solution by the standard volumetric method using potassium permanganate. The amount of calcium so estimated is due to calcium nitrate in the fertilizer.

In Table 1 are given the results of analyses by the new method with a sample prepared from the pure calcium carbonate (G.R.E. Merck) and pure calcium nitrate (G.R.E. Merck). The nitrogen in the sample was present only in the form of calcium nitrate and this was estimated by the method involving reduction with Devarda's alloy and distillation with alkali. In Table 2 are given the results of analyses with three commercial samples of calcium ammonium nitrate fertilizer. The ammoniacal and nitrate nitrogen in these samples were carefully estimated by the alkali distillation and Dev-

arda's alloy reduction-cum-alkali distillation method and the amounts of calcium nitrate were calculated from the excess of nitrate-nitrogen over the ammonical nitrogen. Calcium nitrate was also estimated by the direct method evolved in the present study. The results given in Tables 1 and 2 indicate that this direct method is satisfactory for estimation of calcium nitrate in the nitrolimestone fertilizer.

TABLE 1—ESTIMATION OF CALCIUM NITRATE IN A MIXTURE OF PURE CALCIUM NITRATE AND CALCIUM CARBONATE BY THE NEW METHOD

<i>Calcium Nitrate*</i> wt. %
1.56
1.58
1.57
1.58
1.57
1.56
Average : 1.56
Standard deviation 0.01

\* The value obtained using Devarda's alloy reduction and distillation with alkali = 1.56.

TABLE 2—ESTIMATION OF CALCIUM NITRATE IN CALCIUM AMMONIUM NITRATE

(Calcium Nitrate, wt, %)			
Sample Nos.	Devarda's Alloy Reduction and Distillation with Alkali	New Method	
		Average Value	Standard Deviation
1.	0.84	0.84	0.01
2.	0.99	1.00	0.01
3.	1.24	1.24	0.01

The authors wish to thank Dr. K. R. Chakravorty General Manager, for his interest in this work.

# Effect of Ammonium Nitrate in the Preparation of Nickel Catalyst by Soaking

By

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When nickel nitrate is prepared by dissolving metallic nickel in nitric acid, ammonium nitrate is formed as a reduction product. That the presence of ammonium nitrate has a deleterious effect on the preparation of nickel catalyst by soaking has been indicated here. Even a small concentration of ammonium nitrate in the soaking solution lowers the nickel uptake by the carrier. The results also indicate that high concentration of ammonium nitrate in the soaking solution destroys the mechanical strength of the carrier. It appears that there exists an optimum concentration ratio of nitrates of nickel and ammonium in imparting proper mechanical strength to the nickel catalyst prepared by soaking.

One of the conventional methods for the preparation of supported nickel catalyst is by soaking the porous carrier comprising alumina, alumina-silica and silica in nickel nitrate solution. Nickel nitrate during its preparation gets invariably contaminated with ammonium nitrate. The present investigation is related to the effect of ammonium nitrate, if present in the soaking solution, on nickel uptake by the carrier and finally on the crushing strength of the catalyst.

In general, for large-scale production of nickel nitrate, nickel metal is dissolved in 10-15 per cent nitric acid during which oxides of nitrogen are formed and a part thereof is reduced by hydrogen liberated to form ammonium nitrate. The concentration of the ammonium salt depends on concentration of acid and temperature.

Kalinichenko et al<sup>1</sup> have studied the formation of ammonium nitrate and the effect of introduction of oxygen, hydrogen peroxide and ferric nitrate on the amount of ammonium salts formed. At 40°, 60°, 80° and 100°C with acid concentration 0.46 to 7 N ammonia makes up 90 per cent of the nitric acid reduction product.

For large-scale production of nickel catalyst, it is undesirable from economic point of view to use the nickel nitrate solution obtained directly by reaction of the metal with acid instead of starting with nickel nitrate crystals which involve additional costs for unit operations viz. evaporation, crystallisation, filtration, etc. The soaking solution obtained as above will, however, contain varying concentration of ammonium nitrate.

## Results

(a) *Factors Influencing Ammonium Nitrate Formation:* In order to ascertain the actual amount of ammonium nitrate formed, some experiments were carried out by varying the concentration of nitric acid. In each case, nickel in the form of wire (cut pieces) was added in excess.

The results indicate that the concentration of the ammonium salt increases up to a nitric acid concentration of 25.16 per cent (Table 1). Further increase of acid concentration decreases ammonium content due to the liberation of more of nitrogen oxides.

In another set of experiments the effect of initial ammonium nitrate concentration on its further formation during dissolution of nickel was studied. The results indicated that the formation of ammonium salt is independent of its initial concentration in the acid solution (Table 2).

(b) *Effect of Ammonium Nitrate on Nickel Uptake by the Carrier:* For studying the effect of ammonium nitrate on nickel uptake by the carrier, batches of alumina carrier were prepared under identical conditions. Finely crushed aluminium oxide was treated with nitric acid to give proper plasticity suitable for extrusion. A laboratory model extrusion press with 2:1 compression ratio was used. The material after extrusion cut into proper sizes and kept exposed to atmosphere for 24 hr., followed by oven drying (at 110°C) and curing. In view of the fact that concentration of ammonium nitrate is likely to go on increasing due to repeated soaking of carrier, experiments were performed to

A method for the preparation of active carbon\* from the coke oven acid sludge, a waste material obtained after acid washing of crude benzol, has been developed in this laboratory of the Fertilizer Corporation of India Ltd. This process comprises heating of the acid sludge followed by washing, drying and sizing of the material. The material thus obtained is carbonized and activated.

The process\* of preparation of active carbon is as follows: the raw coke oven acid sludge is heated in a vessel at 100°-200°C till all the fumes are given off. The dry material thus obtained is washed with water till it is free from sulphate ions and dried at 100°-105°C. It is again heated at 300°-400°C in a furnace for 4-5 hr. and then crushed to -7+30 mesh (B.S.) size. It is then carbonized and activated either in a fixed or a fluidized bed by steam or carbon dioxide at 800°-1000°C for 1-4 hr. After activation, the product is quenched in water, treated with dilute hydrochloric acid, and finally washed free of sulphate and dried.

### Storage and Handling of Fertilizers

The application of fertilizers to crops must be made at the proper time in order to ensure an abundant harvest. The farmers are less likely to accept fertilizers in advance of the time when they actually need them, but the manufacturer has to keep his plant in production throughout the year so as to get the greatest benefit from the capital invested and the labour employed. Hence the manufacturer and also the stockist or dealer have to provide storage for the fertilizer. Also, to make fertilizers readily available to the farmers at different regions at reasonable prices, a good distribution system is necessary for which warehouse facilities at widely scattered places should be established.

At present solid fertilizers represent the vast bulk being handled in the different parts of the world. When a large quantity of fertilizers requires to be stored for a long period, it should be done in bulk. Storage of bagged goods for long periods usually involves considerable rebagging before shipment. Solid fertilizers have a tendency to cake or form a hard mass during storage, and depending upon the material involved, time and climatic conditions the caked fertilizer can vary from a light to a very hard mass.

Investigations have been undertaken since 1958 on the various aspects of handling and storage of ferti-

lizers in the Technological wing of the Fertilizer Corporation of India Ltd. at Sindri.

In the first study<sup>1</sup> a simple apparatus has been designed to estimate the caking in fertilizers (Fig. 1). Ammonium nitrate, a very widely used fertilizer, has been studied, because it absorbs moisture and sets to a hard material by the passage of slightly hard moist ammonium nitrate IV  $\longleftrightarrow$  III through 32°C, the transition temperature. A slight change in moisture content has a substantial effect on its caking than a corresponding small change in other factors, such as temperature and pressure. With a view to finding suitable cheap additives to minimize caking of ammonium nitrate, the effect of various additives was studied.

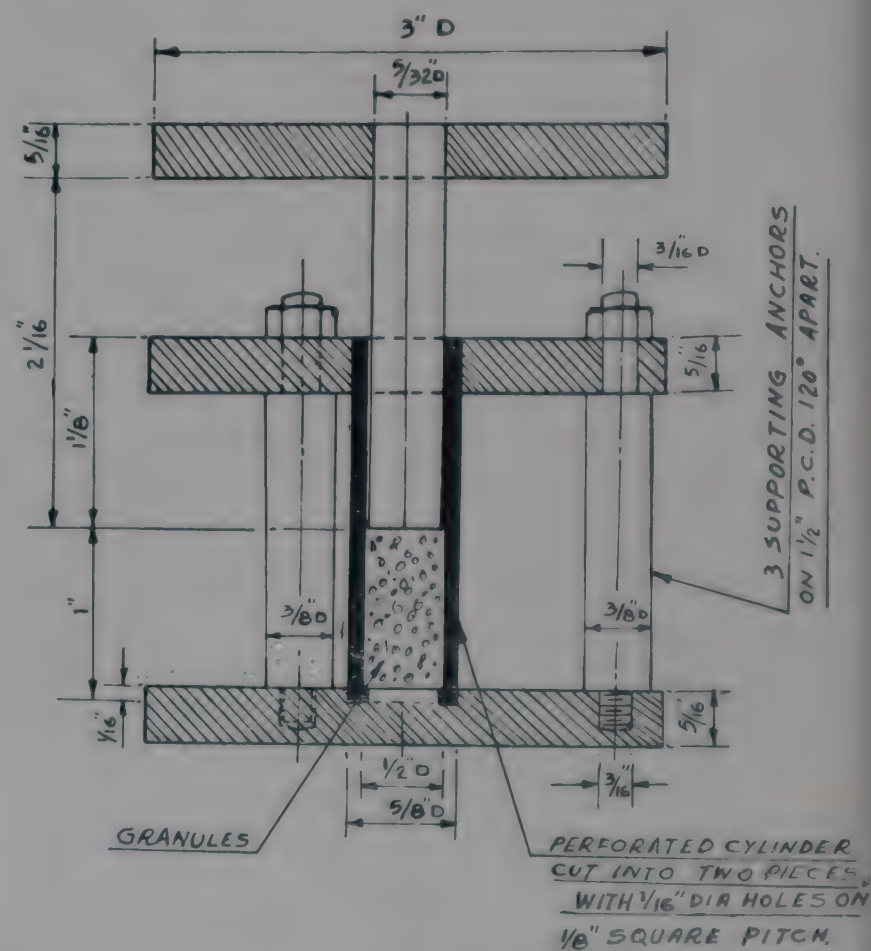


Fig. 1 Caking Test Apparatus.

For the estimation of caking in fertilizers the following procedure was followed: A solution of ammonium nitrate prepared with a minimum amount of water was concentrated on a water-bath to a pasty mass and granulated to -10 +16 B.S. size, and to this conditioning agents, like kieselguhr, chalk, gypsum, rock phosphates, etc. after treatment were added. The sample was then transferred to the caking apparatus consisting of cylindrical perforated stainless tubes of  $\frac{1}{2}$ " dia. supported on a steel frame. By applying the desired pressure on the plunger the sample was pressed in the perforated tube.

\* 'A Process of Preparation of Active Carbon from Coke Oven Acid Sludge' by Dr. K. R. Chakravorty, S. P. Sen and N. B. Bhattacharyya, Indian Pat. No. 84466-D

The perforated tubes were then placed in a constant humidity chamber at 81 per cent relative humidity (R.H.) and pressure was applied on the top of the plunger.

The moisture absorbed was determined by weighing the pellets twice, once when taken out from the humidity chamber and finally after drying it. The crushing strength of pellets was then determined. The stress in pounds per square inch required to crush the pellets was taken as a measure of their relative caking tendency. Similar experiments under different sets of conditions of temperature were conducted for studying the effect of transition on caking (Table 1). The effects of conditioning agents under different pressure, duration and moisture content were also studied (Table 2).

The above study has indicated the following: (1) hard caking occurs in samples which are likely to undergo upward transition; (2) under condition favourable for

downward transition, caking increases only to a small extent; (3) intergranular bonding by ammonium nitrate IV is slightly weaker than the bonding of ammonium nitrate III, and (4) under similar conditions of pressure even if transition does not take place, caking is increased at higher temperature.

As the moisture content increases the granules become more susceptible to pressure or to its duration, and progressively get deformed and forced to come in contact with each other. In this manner the area of contact increases and fertilizer cakes badly.

Of all conditioning materials studied gypsum mixed with nitric acid is the most efficient anti-caking agent. It is in no way inferior to rock phosphate and nitric acid mixture. The impurities, like silica and unreacted calcium sulphate, contribute to the hardening of granules, and thus improve further the keeping quality of ammonium nitrate.

In another investigation<sup>2</sup>, hygroscopicity of the following fertilizer grades of ammonium nitrate, which are in fact ammonium nitrate diluted with inert materials like chalk and kaolin, such as calcium ammonium nitrate (CAN), nitro-kaolin and ammonium nitrate, has been studied (Table 3). CAN and nitro-kaolin have been found to be twice as hygroscopic as ammonium nitrate on the basis of ammonium nitrate content. During the first 24 hr. of exposure to high humidity the samples of CAN absorb larger amount of moisture than ammonium nitrate and later the rate falls, and after a period of 8 days the total moisture content of CAN corresponds to its ammonium nitrate content. Nitro-kaolin also gives similar results. It appears that the diluents like chalk or kaolin are coated with a film of ammonium

TABLE 1—EFFECT OF TRANSITION TEMPERATURE

Sample No.	Temp. of Humidification, °C	Temp. of Drying, °C	Crushing strength, lb./sq. in.	Transition in Ammonium Nitrate
1	25	25	45	No transition
2	25	35	130	Likely transition, IV→III
3	35	35	63	No transition
4	35	25	84	Likely transition, III→IV
5	35	40	78	No transition

TABLE 2—EFFECT OF CONDITIONING AGENTS ON CRUSHING STRENGTH OF PELLETS

Conditioning Agent	Crushing Strength (lb./sq.in.) of Pellets Subjected to Humidification at 25°C and dried at											
	25°C. to a moisture content (%) of						35°C. to a moisture content (%) of					
	0.10	0.18	0.23	0.50	0.70	3.50	0.10	0.18	0.23	0.50	0.70	3.50
Pure ammonium nitrate ..	35	40	45	75	112	180	65	84	130	155	200	350
Kieselguhr, 4% ..	32	35	40	78	120	200	55	74	90	115	148	300
Chalk, 4% ..	38	45	68	120	130	210	65	80	95	130	159	340
Kaolin, 4% ..	35	37	42	115	125	205	60	75	90	125	155	320
Gypsum, 4% ..	38	42	49	110	115	205	63	76	100	130	175	360
Gypsum, 2% ..	36	38	46	85	118	160	64	89	110	140	170	330
Tricalcium phosphate, 4% ..	35	38	45	35	130	215	58	76	93	120	160	345
Calcium nitrate, 0.5% ..	25	38	45	69	98	150	50	55	70	95	110	190
Gypsum, 2.5% + nitric acid	20	35	40	70	93	155	45	48	60	80	95	175
Rock phosphate, 2.5% + nitric acid ..	25	40	42	75	95	160	48	50	60	90	105	180

TABLE 3—HYGROSCOPICITY TESTS

(Samples exposed to 81% R.H. at 25°C.; wt. of sample taken for test, 1.0 g.; granule size, -10+16 mesh)

Period of Exposure, hr	Moisture Absorbed by			
	Ammonium nitrate, %	Nitro-kaolin (60 : 40), %	Nitro-chalk (60 : 40), %	Nitro-chalk + chalk (60 : 34 : 6), %
12	8.7	12.5 (21.0)*	14.5 (24.0)*	9.5
24	13.5	15.5 (26.0)	14.0 (23.0)	19.5
36	8.8	9.5 (16.0)	8.8 (14.6)	8.0
48	17.0	7.1 (12.0)	6.6 (11.0)	7.0
60	16.4	2.1 (3.5)	1.7 (3.0)	1.5
72	—	—	—	—
84	12.8	3.7 (6.0)	3.8 (6.3)	3.6
96	4.3	0.4 (0.7)	0.3 (0.5)	0.2
Total	81.5	50.8 (85.0)	49.7 (83.0)	49.3

\* Figures in parentheses relate to values on the basis of ammonium nitrate content.

nitrate and the surface area thus exposed is high. Conditioning of CAN by chalk to the extent of 6 per cent decreases the rate of moisture absorption to a small extent. As the duration of exposure to high humidity increases, the conditioning agent fails to protect the granules and thus the conditioned samples fare no better than the unconditioned ones.

On studying the caking behaviour of the fertilizer-grade ammonium nitrate, the results indicated some important differences in the caking of CAN and ammonium nitrate. The conditioning agents normally effective in minimizing caking of ammonium nitrate do not reduce the caking of CAN. There is only a slight increase in the crushing strength if the conditions of temperature are such that the sample is likely to undergo an upward transition IV—→ III, whereas in the case of ammonium nitrate the crushing strength increases to the extent of two to three times when the sample is dried above 32°C. The slight increase in caking may be attributed to increase in the solubility of ammonium nitrate.

The absence of hard caking in CAN has been attributed to the fact that unlike ammonium nitrate granules, the porosity of CAN granules is not significantly altered at the transition point, and consequently the moisture held inside is not released when the sample undergoes an upward transition.

In another investigation, various inert materials have been studied for use as diluent for ammonium nitrate. The hygroscopicity absorption capacity for saturated ammonium nitrate and caking tendencies of the various samples of ammonium nitrate-inert mixture have also determined.<sup>3</sup>

In carrying out the experiments, ammonium nitrate was dissolved in a minimum amount of water and 40 per cent of the powdered diluent (-200 B.S. mesh) was added. The slurry was heated over a water bath, and when formed to a paste-like consistency it was granulated to -8+16 mesh and dried to a near-dry mass to which the conditioning agent was added, so that the final product contains 20.5 per cent nitrogen. An weighed amount of dried sample of the fertilizer-inert mixture was exposed to an atmosphere of constant humidity over a saturated solution of ammonium sulphate containing an excess of salt, and its hygroscopicity was determined. The caking characteristics of another sample were determined (Fig. 1).

The above study has indicated that nitro-clay (ammonium nitrate with clay) is the most hygroscopic, and the difference in the rate of moisture absorption by ammonium nitrate diluted with different inert materials is due to the difference in the surface area of ammonium nitrate made available in the presence of inert diluents.

This conclusion is substantiated by bulk density measurements—the lower the bulk density of the diluent the higher the hygroscopicity of the diluted fertilizer.

While clay increases the caking as well as hygroscopicity of the mixtures as compared with mixtures containing chalk or limestone, the hygroscopicity of diluted ammonium nitrate is least in the case of ammonium nitrate-gypsum mixture, but its caking characteristics are inferior to those of ammonium nitrate-limestone.

In the fourth study, bags with different moisture-proof linings viz. polyethylene liner, crepe paper pasted with bitumen to jute, two plies of bagging paper laminated and pasted with bitumen, etc. have been tested for their moisture impermeability and mechanical strength after storage for 4 months<sup>1</sup>. The idea was to determine the most suitable bag for bagging hygroscopic fertilizers. The relative effectiveness of such bags was evaluated on the basis of moisture content of urea

before and after test, caking of urea and the physical conditions of the liners.

Prilled urea was filled into the bags which were then stitched and the bags then placed under pressure (under 350 Kg. wt.) in a well-ventilated warehouse. At various intervals, the moisture content of the urea was determined. The mechanical strength of the liner was determined by dropping the bags five times from 6 ft. height and stacking them (Table 4).

The results indicated the following: (i) polythene-lined jute bags are superior to polyvinylidene chloride coated or paper-lined jute bags; (2) urea stored in polythene-lined bags absorbed minimum moisture and caked less, and the bags could withstand rough handling better; (3) polythene liners, stitched to jute bags, proved to be better than the loosely inserted ones, their thickness should be at least 0.002 in.; and (4) the liner and the jute should be folded and doubly stitched

TABLE 4—STORAGE TESTS

Liner	Condition of bag after test	Moisture content of urea* after test %	Lump formation % (2 mesh)	Type of Lump	Bags subjected to rough handling			
					Condition of bag after test	Moisture content of urea* after test %	Lump formation % (2 mesh)	Type of lump
Jute bag painted with polyvinylidene chloride	Bags completely moist; slightly damaged	1.61	50	Hard	Bags completely moist; damaged	1.75	57	Hard
Two-ply bagging paper bonded with bitumen pasted to jute bag	„	1.20	40	„	„	1.51	50	„
Polythene liner (0.001 in. thick) loosely inserted in jute bag.	Bags dry; liners intact	0.41	36	Soft	Bags moist; liners torn	0.99	45	Soft
Polythene liner (0.002 in. thick) loosely inserted in jute bag	„	0.16	18	„	„	0.26	23	„
Polythene liner (0.003 in. thick) stitched to jute bag	„	0.10	5	„	Bags dry; liners intact	0.15	7	„
Polythene liner (0.002 in. thick) stitched to jute bag	„	0.15	10	„	„	0.10	12	„
Crepe paper pasted to jute with bitumen.	Bags partially moist; liners damaged	1.10	45	Hard	Bags moist; liners torn	1.61	55	Hard
Polythene liner (0.002 in. thick) double-stitched to jute bag.	Bags dry; liners intact	0.10	—	—	Bags dry; liners intact	0.15	10	Soft
Control (ordinary jute bag)	Bags completely moist	1.24	60	Hard	„	—	—	—

\* Initial moisture content of urea, 0.03 per cent.

so that there is less likelihood of moisture penetrating through the sides.

This problem when undertaken was of considerable importance in view of the fact that hygroscopic fertilizers like urea and ammonium sulphate-nitrate were going to be produced at Sindri and suitable moisture-proof bags were necessary for bagging such fertilizers. In developed countries the most common moisture-proof bags in use are multiwall paper bags. These consist of three to six plies of Kraft paper with one or two layers of bitumen between them. These bags are unsuitable and are likely to create during handling problems—peculiar problems prevalent in this country—even if they are available at a reasonable price.

These investigations have led the FCI to use polyethylene-lined jute bags for bagging urea, ammonium sulphate nitrate and calcium ammonium nitrate.

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#### Filtration Characteristics of Gypsum Reaction Magmas

In the gypsum process of ammonium sulphate manufacture, a solution of ammonium carbonate is allowed to react with powdered gypsum at 65°-70°C, but this process is not economical with certain varieties of gypsum yielding magmas with poor filtration characteristics and causing operational difficulties. The filtration rate of the slurry (or magma) falls with decrease in the particle size of the solid present, and the presence of a small amount of slimy impurity may severely impair the filterability of an otherwise good-filtering material. Studies have therefore been carried out in this laboratory\* on different varieties of gypsum with a view to correlate the filtration characteristics of magmas produced during the reaction of gypsum and ammonium carbonate with the impurities present in gypsum and particle size of chalk produced.

Gypsum samples from Khewra (W. Punjab, Pakistan), Tiruchirapalli (Madras), Jamsar and Kavas (both in Rajasthan) were subjected to chemical and x-ray analyses with a view to identifying the phases present as impurities. The particle size distribution of these samples as well as of the solids obtained after their reaction with

ammonium carbonate was determined. Gypsum was allowed to react at 68°-70°C with ammonium carbonate solution, containing 18.0 g. ammonia and 23.6 g./CO<sub>2</sub>/100 ml. in a small steam-heated reaction vessel of stainless steel with an agitator inside rotating at 90 r.p.m. for 2 hr. The magma was filtered under vacuum and the filtration time was noted. The cake was washed with distilled water at 90°C and its ammonium sulphate and total SO<sub>3</sub> estimated, from which the conversion of gypsum to ammonium sulphate was calculated. X-ray diagrams of the impurities in four gypsum samples were taken, and the samples were also observed under a microscope. Particle size analysis was made microscopically by measuring Martin's diameter of nearly three to eight thousand particles for each variety and taking average values.

This study has indicated that Khewra gypsum is the purest (CaSO<sub>4</sub> 78.08 per cent) and the magma produced from it has the best filterability; of course the conversion in all case is high (Table 1). Although the Kavas gypsum is of a lower grade (CaSO<sub>4</sub> 60.76 per cent), the magma obtained from it has a far better filterability than that from the Tiruchirapalli variety.

TABLE 1—BEHAVIOUR OF DIFFERENT SAMPLES OF GYPSUM ON REACTION WITH AMMONIUM CARBONATE

Gypsum sample	Filterability of magma*	Average conversion
Pakistan	41.2	97.5
Jamsar	61.5	97.7
Tiruchirapalli	151.7	97.9
Kavas	68.4	98.0

\* Expressed as average period (in sec.) for complete filtration.

The chalk obtained from Khewra gypsum has the finest size distribution (Table 2). The size distributions of chalk samples from Jamsar and Tiruchirapalli gypsum are of the same order, they are coarser than the chalk from the Pakistani gypsum but finer than that from Kavas sample. In the sub-sieve range, however, the chalk from Tiruchirapalli gypsum has the finest size distribution, the chalk from the Pakistani gypsum being slightly coarser.

No definite correlation has been observed between the size analyses of chalk and gypsum samples and the filterabilities of magmas produced after reaction. The chalk slurry obtained from the Pakistani gypsum has a better filterability than the one obtained from Kavas or Jamsar gypsum, although the chalks from these two varieties have coarser size distributions than that from

\* Roy, A. K., Banerjee, K. C., Bardhan, M. K. & Chakravorty, K. R., *J. sci. & industr. Res.*, 20D (1961), 361-365.

TABLE 2—SIZE ANALYSES OF GYPSUM AND CHALK SAMPLES  
(Values represent cumulative wt per cent below the particular size range)

Size	Pakistan sample		Jamsar sample		Tiruchirapalli sample		Kavas sample	
	Gypsum	Chalk	Gypsum	Chalk	Gypsum	Chalk	Gypsum	Chalk
100 mesh (B.S.S.)	98.8	92.7	74.9	83.9	74.6	89.7	76.6	81.6
150 mesh (B.S.S.)	89.0	87.3	56.2	75.2	56.2	81.9	53.3	62.0
200 mesh (B.S.S.)	84.7	83.8	47.7	70.7	47.5	77.5	43.9	53.3
28.0 $\mu$	13.8	42.6	4.8	19.4	14.8	42.2	8.8	18.6
19.8 $\mu$	4.2	12.1	4.6	4.2	4.1	20.6	4.2	3.4
14.0 $\mu$	1.4	4.5	1.6	2.5	1.9	12.5	2.8	1.5
9.9 $\mu$	1.0	1.9	0.8	1.6	1.3	8.1	1.9	0.9
7.0 $\mu$	1.0	0.9	0.7	1.2	1.0	5.3	1.5	0.8

the Pakistani variety, both in the sieve and sub sieve ranges. The chalk slurry from Tiruchirapalli gypsum has the worst filterability.

The results of x-ray analyses of the impurities indicated that  $\alpha$ -quartz and calcite were the major phases present in the Jamsar and Kavas varieties, and a third phase—an aluminium silicate—has also been indicated, which is perhaps a crystalline matter of the Kyanite type. Both quartz and calcite are known to be good-filtering constituents, and therefore it is not surprising that the Kavas gypsum with its low purity does not give filtration trouble. The exceptionally good filterability of the magma from the Pakistani gypsum, in spite of the finer size distributions of the gypsum and chalk particles, may be at least in part due to the presence of dolomite as the single impurity phase. In addition to  $\alpha$ -quartz, montmorillonite clay was identified in Tiruchirapalli gypsum, and the presence of the latter explains the bad filterability of magma obtained from this variety of gypsum.

### Extraction of Sulphur From Spent Oxide

Iron oxide either naturally obtained as bog iron ore or prepared products like luxmasse are normally used for the desulphurization of industrial gases like coal gas, water gas, producer gas, etc. The principal reaction taking place in the desulphurization process is the combination of the hydrogen sulphide of the gas with the iron oxide in the mass forming iron sulphide, which in turn is oxidized to ferric oxide with simultaneous precipitation of free sulphur by oxygen present. This takes place either *in situ* or by exposing it to the atmosphere\*.

The mass unsuitable for further use in the desulphurization of the gases generally contains 40 to 60 per cent free sulphur on the dry original oxide basis, and therefore the sulphur in the spent mass is worth recovery. Already some processes for the recovery of this sulphur are in existence, but they involve either costly chemicals or hazard, and in some cases the recovery is even low.

A process has been developed in this laboratory for the extraction of sulphur from the spent iron oxide desulphurization mass and at the same time to produce a mass of increased desulphurization capacity.† The extracting medium is the crude concentrated ammoniacal liquor, which is readily available from coke ovens but, if not available, can be prepared by condensing the vapours from ammonia distillation. The crude concentrated ammonia liquor in general contains the following: ammonia (15 to 20 per cent), hydrogen sulphide (2 to 4 per cent) and varying amounts of carbon dioxide, cyanide, pyridine bases, phenols, organic matter, etc.

The process is as follows: the spent iron oxide, free from the lighting materials like the wood shavings, etc., is mixed with ammonia liquor in the proportion 10 to 50 litres per kg of the mass in a paddle mixer, or alternatively the liquor is allowed to percolate through a tower filled with the spent iron oxide mass, for 30 to 60 minutes. The liquor is then separated by filtration and the residual mass washed free of ammonia with water. The spent oxide is then exposed to atmosphere with occasional raking for oxidation for about

† 'A Process for Extraction of Sulphur from Spent Iron Oxide & Revivification of its Desulphurization Capacity' Indian Patent No. 80817 (Inventors: Dr. K. R. Chakravorty, B. K. Dutta, A. C. Nanda, A. C. Srivastava & C. Sarkar).

\* Technol., 1 (1964), 2, 41-42.

24 hr. The filtrate and washings of the mass are then distilled with steam to recover completely ammonia, and the sulphur is separated from the residual liquor by filtration.

The composition of the revived spent oxide is as follows:  $\text{Fe}_2\text{O}_3$  40 to 50 (w/w), sulphur 5 to 7 per cent (w/w). Its  $\text{H}_2\text{S}$  absorption capacity is 2.6 to 2.8 mols of  $\text{H}_2\text{S}_4$ /mol of  $\text{Fe}_2\text{O}_3$ . It can be used again for desulphurization of gases.

Some of the advantages of this process are the follow-

ing: (1) sulphur recovered is in the form of a fine powder of about 98 per cent purity, obviously suitable for various chemical and agricultural uses; (2) the desulphurization capacity of the revived spent iron oxide is even higher than that of the oxide mass; (3) the recovered ammoniacal liquor is completely free from cyanides containing less  $\text{H}_2\text{S}$  than the original liquor and can, therefore, be used for the preparation of ammonium salts; (4) the crude ammonical liquor available as a by-product in coke oven plant finds a suitable use.

# Notes & News

## Improvements in Fertilizer Technology

While organizations like Texaco, W. R. Grace, Du Pont, Hercules, TVA in the USA and Shell, ICI, Pechiney, ONIA and Montecatini in Europe have contributed new developments in fertilizer technology, engineering firms have been the leading contributors of improvement in this field. The manufacture of fertilizer is a capital intensive industry having the ratio of fixed charges to the manufacturing cost of ammonia or urea in the order of 35 to 45 per cent. At present there are five routes to synthesis gas production which have commercial importance viz. steam reforming, partial oxidation, water gas production, electrolysis and hydrogen-rich off-gas treatment, of which the first two have great future potentials. Since the World War II, the trend has been away from the use of solid fuels, and during the last ten years the same has been towards the use of natural gas. Natural gas is converted to a hydrogen-rich gas by a catalytic process—the gas reform process in conjunction with the water-gas shift reaction. Other sources for gas production are coke oven gas, refinery gas, acetylene off-gas from which hydrogen is extracted.

The present trend in gas reform processes has been towards the use of high pressure in the reform furnace. The original processes were based on the catalytic reaction between methane and steam at 1700°F and 20-30 lb/sq.in, while recently Chemico and Foster Wheeler have installed reformers operating at 300 lb/sq.in. The high pressure process provides significant savings in the cost of production of ammonia because of the following: the product gas from the reformer being at a high pressure does not necessitate a higher compressor horse power; natural gas, generally available at high pressure, can be utilized directly; better heat recovery from steam-condensate of the process gas; small size equipment and piping can be used; carbon monoxide conversion is more efficient, and carbon dioxide removal system is more efficient and compact. The disadvantage of unfavourable methane equilibrium in operating at higher pressure can be overcome by higher temperature in furnaces.

In the partial-oxidation process, hydrocarbons are oxidized under pressure in a flame reaction with either oxygen or enriched air which is non-catalytic. There are a variety of this process now available viz. Texaco, Shell, Kopper-Totzek and ONIA. Its advantage is its feedstock flexibility. It can handle gases, liquid fuels upto Bunker C and even solids. Both Texaco and Shell processes operate at 450 lb/sq. in. at which the subsequent steps of CO<sub>2</sub> conversion and CO<sub>2</sub> removal can also be operated under pressure with better efficiencies in less costly and more compact equipment.

While both the steam-naphtha reforming processes viz. ICI and Chemico, operate at pressures around 300 lb/sq. in., the former is a two-stage one—air addition being done in the second stage—and the latter an one-step process in which air, steam and naphtha are simultaneously reacted in a single catalytic reforming unit. Since this process has lower investment and operating costs than the partial oxidation it could displace the latter in many countries where naphtha is in excess supply. The cost for the naphtha reform plant is about 15 per cent higher than a natural gas-based steam reform plant of the same capacity. The following methods have potentiality for the future: (1) use of internal combustion engines with directly usable power and (2) use of atomic energy for the chemical reactions of ammonia synthesis.

Recent developments in carbon monoxide conversion relate mainly to catalysts—by Girdler, CCI and Svenska—of higher activity operating at lower temperature. Since the CO-conversion equilibrium yields lower carbon monoxide at lower temperature, its removal is more efficient with the newer catalysts operating at higher velocities. Changes in carbon monoxide converter design as well as the heat saturator towers in tandem with the CO-OK units are recent developments. With such catalysts, the traditional two-stage carbon monoxide conversion step with two carbon dioxide removal units has been replaced by a single CO-OX unit, using two catalyst beds with interquench and one carbon

dioxide removal unit, yielding considerable savings in investment and utilities.

About carbon dioxide removal, the cold water scrubbing has given way to more efficient and compact monoethanolamines (MEA) system, and later hot carbonate system by Chemico. Improvements in the hot carbonate system include Giamarco using arsenic type additive and the Catacarb processes. With high pressure gas reforming processes and single stage CO-OX unit, heat economy is better with MEA system, while some solvent processes are also being developed by Shell and others. The methanation process has also become economically attractive, while liquid nitrogen is also being used for the final clean-up of synthesis gas for its CO and CH<sub>4</sub> content.

About ammonia synthesis, processes like Kellogg, Chemico-NEC and Fauser are preferred over the higher pressure ones. Cynamid and Topsoe have introduced triple-promoted iron oxide, while Chemico have introduced a triple-tube in the catalyst basket design in their converter. Another step was the use of a steam-recovery stem in the converter system. The use of compressors with integrated services helps to reduce the cost of compression, and the size of the converters has increased from 120 to 600 tons/day.

Improvements in urea technology have been on the following lines: new total recycle processes such as liquid-recycle technique, lower cost materials of construction, and larger capacity single-train units. Some alternate methods of producing urea from COS and ammonia have been patented, while Monsanto has a patent using sulphur, ammonia and carbon oxides.

[S. Strelzoff & S. Vasan, Chem. Engng. Pro., 59 (1963), 11, 60-65]

## New Catalyst for Steam-Hydrocarbon Refining

In the production of hydrogen at high pressure by catalytic steam-reforming of hydrocarbons, carbon deposition on the catalyst is a nuisance. For its removal excessive steam is required. However, a

new catalyst (KSR-3), developed by M. W. Kellogg Co. of U. K., permits a four-fold reduction in steam requirement for carbon-free operation.

With operating temperatures ranging from 650-1100°F for the inlet and 1300-1450°F for the outlet gases and pressures not exceeding 255 psig, two conventional steam-reforming catalysts give large differences in limiting steam/carbon ratio with various feedstocks tested and generally tended to show a large pressure effect, whereas KSR-3 was almost independent of pressure upto 700 psig. The type of feedstock also did not significantly influence the limiting steam/carbon ratio (which was much less than that for other two catalysts) in the case of KSR-3 showing thereby its feedstock flexibility. Even with feeds ranging upto a molecular weight of 310, this catalyst gives a marked reduction in steam requirement. Ageing study in a commercial reformer showed that while the conventional reforming catalyst gets broken up and powdered, KSR-3 still remains in an excellent physical condition.

Pilot plant studies with this catalyst with different feedstocks over a pressure range 50-600 psig, outlet temperature 1300°-1500°F and steam/carbon ratio 1.0-9.0 have indicated that the conversion of naphtha as well as olefinic refinery gases is 100 per cent. With natural gas as feedstock, KSR-3 has a higher methane-reforming activity than a commercial catalyst.

In view of its satisfactory performance, good strength and ageing characteristics and high feedstock flexibility, KSR-3 has already come into commercial use in a 300 ton/day ammonia plant at Joplin, Missouri, and a 100 ton/day plant at Pryor, Oklahoma.

[Research & Indus., 9 (1964), 112]

#### Developments in Urea Manufacture

Recycling is the key to economic production of urea, and a variety of techniques are available viz. recycling of ammonia-carbon dioxide gas mixture at high temperature, recycling of ammonia alone in the liquid state or of both reactants in solution or in suspension. Temperature is an important factor.

The intrinsic difficulties of compression of gaseous ammonia-carbon dioxide mixtures has led to the idea of separation by selective absorption of the two gases which are recompressed separately in the reaction chamber. Recycling in aqueous solution is particularly advantageous and has been

adopted at the Novara works of Montecatini. The working temperature is 180-190°C and the pressure about 200 atm. The plant being of stainless steel, there are no corrosion problems. The aqueous solution of urea, ammonium carbonate and ammonia leaving the reactor is subjected to two successive let-downs accompanied by heating which leads to decomposition of the ammonium carbonate and to distillation of its decomposition products.

The two decomposition/distillation steps lead to nearly complete separation of the ammonia and carbon dioxide not converted in the reactor. The small residual quantities can usually be recovered by fractional condensation of the vapours separated during subsequent concentration of the aqueous urea solution, the fraction richer in ammonia being returned to the system. By this means, conversion yields very close to 100 per cent are achieved.

The aqueous urea solution after concentration is sent either to the granulating or crystallizing plant. In the former case, it is first subjected to a second vacuum concentration prior to granulation. The vapours separated in the two decomposition/distillation steps are passed to two condensers/absorbers at medium and low pressure where the water present in the vapours is condensed and the ammonia and carbon dioxide are absorbed. An aqueous solution of ammonium carbonate and ammonia is ultimately obtained and recycled.

The most interesting feature here in the recovery of the heat developed in the medium-pressure condenser/absorber and its direct utilization in the low pressure decomposition/distillation steps which permit of condensation and absorption of the vapours separated in the first step at a temperature considerably higher than that of the low pressure decomposition/distillation step so that the heat developed in the first step can be utilized in the second.

[Indus. Chem., 40 (1964), 215]

#### Continuous Process for Calcium Ammonium Nitrate

Calcium ammonium nitrate (CAN), which can have as high as 26 per cent nitrogen, is a fertilizer having good storage properties. Messrs Pintsch-Bamag A. G. have recently developed a continuous process for CAN manufacture. In this process 55 per cent nitric acid is neutralized with ammonia to obtain ammonium nitrate as intermediate the desired nitrogen content

(17.5, 20.5 or 26 per cent) of the final product being obtained by adding varying amounts of powdered limestone.

Liquid ammonia is gasified in an evaporator and led to the main neutralizer. Nitric acid of not under 50 per cent strength is then fed to the main neutralizer forming ammonium nitrate. A secondary neutralizer removes the fumes from the first neutralizer and the heat resulting from the neutralization of nitric acid evaporates the greater part of the water entering with the acid and thereby concentrates the liquor to 82-84 per cent. Any resulting vapour is precipitated with coolant water in the surface condenser. An automatic pH control ensures that ammonium nitrate obtained is as neutral as possible.

Ammonium nitrate is concentrated in a vacuum evaporator unit to about 96-97 per cent. It is then mixed with finely ground limestone from an automatic weigher. The mixture is then granulated and the product then passed through a drying drum to a sieving unit. The sieved granules with diameter size 1 to 5 mm. pass through a coolant drum to a temperature of under 30°C to prevent crystallization and obtain good storability property. Crystallization of the ammonium nitrate liquor is also possible by the crystallizer roller or tower process developed by Pintsch-Bamag.

[Nitrogen, No. 28, (1964), 28-29].

#### ICI Catalyst for Ammonia Synthesis

The new catalyst 35.4 consists essentially of magnetic ( $\text{Fe}_3\text{O}_4$ ) multipromoted by the addition of alumina, calcium, and potash, and some other substances including silica in controlled amounts. It is available in the form of hard attrition-resistant fused granules in the size range 3 to 9 mm., having 167 lb/cft. bulk density.

The threshold temperature at which ICI catalyst 35.4 becomes active is about 350°C. At higher temperatures the activity is greater, but the equilibrium ammonia yield and consequently the reaction driving force are reduced, the net forward reaction rate increases with temperature to pass through a maximum and then falls to zero when equilibrium is reached.

The performance of the catalyst depends on converter designs. A typical catalyst basket is the tube-cooled type in which reaction gas flows through the catalyst counter-current to the gas flow in the cooling tubes.

Under the most favourably operating conditions as little as 30 per cent reduction

in catalyst activity takes place during the first three years of operation. In plants, however, the reduction in activity is 40 to 50 per cent due partly to the high concentration of catalyst poisons in the inlet gas and partly to overheating of the catalyst.

[Nitrogen, No. 28, (1964), 30-31]

### Prilled NPK Fertilizers

Stamicarbon NV Geleen Netherlands has developed a process, whereby prills containing nitrogen, phosphorus and potassium can be prepared. A melt which contains all the three elements is prepared by appropriate adjustment of pH with the help of a strong acid added to the melt before the potassium salt. The melt can be pumped easily and contains 14 per cent each of N,  $P_2O_5$  and  $K_2O$ . Use of potassium sulphate in preference to potassium chloride has been advocated.

[Phosphorus & Potassium, No. 6, (1963), 48-49; Abstr. Roy, M. R., Abstracts, July (1964), 1, P & D Division, F. C. I. Ltd.]

### Largest Phosphoric Acid Reactor

The world's biggest phosphoric acid reactor has come into production at the ICI's Billingham plant replacing a system requiring five reaction vessels. The new plant marks the first stage in the rationalization of fertilizer production at Billingham. With an associated Prayon filter, it forms a highly compact unit ensuring a more efficient extraction of phosphate from imported rock. The reactor made of mild steel is 16 ft. high and 40 ft. in diameter, butyl-lined and internally faced with carbon bricks which were joined with phenol formaldehyde resin cement.

### Economy in Phosphate Manufacture

Submerged combustion provides the clue to the production of a concentrated phosphoric acid (Anhydrous Liquid Phosphate), which is able to provide concentrated ammonium phosphate solutions, in which all the impurities remain in solution. The ALP can also be used to make high analysis granular solids that are tough, dust-free and less expensive to make than one based on 52-54 per cent acid. The features of this process, developed by Collier Carbon & Chemical Corpr., include a natural gas burner with a converging-diverging throat and very short residence time for the evaporation of the wet process acid to be concentration being controlled by the temperature of the combustion gases.

The combination of incoming feed, pressure from combustion gases and ebullient boiling of the liquid forces the concentrated product to rise through an annular channel into a gas liquid disengaging zone. In this widened zone, volatile off-gases boiling from the mixture rise upward to a mist separator, which agglomerates liquid droplets which join the main stream of concentrated acid en route to a cooler. The hot gases meanwhile are water-sprayed and then filtered before discharging through a stack. Overall phosphorus pentoxide recovery in the plant is better than 99.8 per cent.

The other benefits include appreciable reductions in the cost of transport, tank tar cleaning, and in the manufacture of liquid and solid fertilizers—all these for the modest penalty of a small additional cost of concentrating the acid.

The finished product ALP is a dark brown or green liquid; relative to ordinary 52 per cent wet process acid it is fairly non-corrosive, viscous and heavy. It is pumpable at 70°F.

[Chem. Engng., 71 (1964), 1, 26-27]

### ICI Increases Fertilizer Production

Imperial Chemical Industries have announced a £20 million investment for another major expansion of its Agricultural division's fertilizer production to meet increasing demand in home and export markets. This means they are to be the largest single producer of ammonia in the world. This programme includes a plant now being completed to make a new high-concentration nitrogen fertilizer, and the conversion of existing plant to manufacture compound fertilizers of higher concentration. A large urea plant is to come into production in 1966, which will require a further immediate expansion of ammonia production.

A new 300,000 tons per year prilled ammonium nitrate plant at Severnside (near Bristol) will provide in early 1965 a highly concentrated and high-quality fertilizer, containing 34.5 per cent nitrogen, the production of which will be further increased.

A new, more concentrated compound fertilizer, containing nitrogen (15), phosphate (15) and potash (21 per cent), will become available in increasing quantities during 1964-65. The plant at the Billingham works will also be converted to manufacture this compound fertilizer.

The new urea plant at Billingham, which will be the largest in the world with a capacity of about 350,000 tons/year, will go into production in 1966. Another new ammonia plant, with a capacity of at least 300,000 tons a year using the ICI pressure steam-reforming process, is to be built.

[Chem. & Indus., No. 23, (1964), 989]

### Compound Fertilizer

Scottish Agricultural Industries (SAI) at Leith have developed a process which consists of two drums revolving one inside the other, in which sulphuric, nitric and phosphoric acids are reacted with ammonia to give a dry, granular product built up in layers on an almost perfect spherical shape. The chemical energy liberated during the reactions is utilized to evaporate all the water present giving the dry granular product. The spherical granule so produced is a complete synthetic fertiliser in one process circle, including potassium salts.

Ammonia for the process is stored in two 36.5 ft. spheres under a pressure of 45 psi and nitric acid of 70 per cent is used. The two acids viz. phosphoric and nitric acids and ammonia together with crystalline potash are accurately metered and fed in the correct proportions, according to the analysis of the end-product, into two concentrically rotating granulating drums. As they pass round the cycle, the particles are coated in turn by a layer of phosphoric and nitric acids, these being immediately neutralised by ammonia. Potash salts are also included during the cycle.

SAI intend to produce only two analyses in the first year viz. SAI No. 1 of high potash content with a plant food ratio of 1 : 1 : 1.33 and SAI No. 2, 2 : 1 : 1. Actual  $N/P_2O_5/K_2O$  ratios are 16/16/21 per cent and 23/11.5/11.5 per cent respectively. These are claimed to be 25-30 per cent more concentrated than previous products.

The granules are coated with a specially developed non-toxic, non-corrosive powder to ensure free flowing properties and are packed in polythene sacks.

[Chem. Trade J. & Chem. Engr., 154(1964), 4016, 774]

### Fertilizer as Power Station By-Product

Fertilizer as a by-product of electric power generation is foreseen by engineers at the Westinghouse Research Laboratory where work is being done on magnetohydrodynamic (MHD) generation of electric

city. Dr. W. T. Lindsay has proposed that nitrogen might be fixed and nitrogen compounds recovered during MHD power generation, and laboratory experiments have confirmed that the process is feasible. At the moment a generator at the laboratories is producing electricity and fertilizers simultaneously.

The MHD generator operates at temperatures of about 4500°F and at these temperatures the nitrogen and oxygen in air combine to form oxides of nitrogen which can be recovered, indirectly, as nitrates. The generator substitutes a high speed, high temperature gas or plasma for the rotating copper coils in the conventional electric generator.

[Chem. Trade J. & Chem. Engr., 154 (1964), 4014, 680.]

### Hydrogen Recovery

New processes for recovery of high purity hydrogen from gas streams have been developed by Petrocarbon Developments Ltd. The processes are of a low temperature single stage type and are said to be able to recover hydrogen from impurities, such as those of an inorganic nature as formed in ammonia synthesis purge gas or organic as in refinery off-gas, very simply. The cost of recovery is claimed to be substantially less than producing the hydrogen by other known methods.

[Chem. Trade J. & Chem. Engr., 154 (1964), 4616, 770]

### World's Largest Ammonia Plant

Federation Chemicals Ltd., has placed on stream at Point Lisas, Trinidad, a \$ 21,500,000 plant with an annual rated production of 235,000 tons of anhydrous ammonia. Low-cost natural gas and deep water are cited by W. R. Grace & Co., the principal stock-holder (49 per cent) in the Federation Chemicals new venture, as the primary reasons for choosing Trinidad for this operation. Capable of feeding the plants, old and new, with 30 million cfd of natural gas are lines brought in from the Trinidad fields of Texaco and Shell. Built by Chemico International, this single-line plant has the largest ammonia converter ever built anywhere—a 283 ton unit. The finished product ammonia is designed to be shipped abroad in two specially-built tankers—each of 9,000 tons capacity—loaded in less than 20 hr each.

The natural gas is cracked over a nickel catalyst by the steam reform process to yield hydrogen, carbon monoxide and

carbon dioxide. The gases are then passed to a second reforming process where air is introduced and combustion takes place removing the free oxygen from the gas by conversion to water. Carbon monoxide is shifted to carbon dioxide by the addition of steam and passing over a catalyst. The carbon dioxide and the small remaining quantity of carbon monoxide are removed from the gas stream by scrubbing with monoethanolamine, and the carbon dioxide is transferred to the urea plant for further processing.

[Chem. Weekly, 9 (1964), 5, 8-12]

### A New Phosphate Fertilizer

There are countries who do not themselves possess superphosphate factories and where the importation and consumption of fertilizer are restricted, mainly on economic grounds. In these circumstances there may well be a considerable interest in the local fabrication of less expensive substitute. Investigations in the Wisconsin University (USA), Paris, Australia and Senegal have been carried on the solubilisation of rock phosphate by adding sulphur.

The Wisconsin University work involves the addition of rock phosphate to molten sulphur, admixture and granulation. The smaller the rock phosphate-sulphur granule size, the more rapid was the oxidation of the sulphur to sulphuric acid and subsequent action in solubilising the phosphorus. The granules were much more effective in supplying phosphorus to crops on acid soils than on alkaline soils. The lower efficiency on alkaline soils was due to the dissipation of appreciable amounts of sulphuric acid by the soil around the granule before it could react with the rock phosphate. This treatment has resulted in higher uptake of total phosphorus by the crop and higher percentage of sulphur in the tissue. Dr. Attoe's work has indicated that a mixture of rock phosphate in molten sulphur may provide an effective source of phosphorus.

At the Institut de Recherches pour les Huiles et Oleagineux (Paris), work has been carried out since 1959 on the solubilization of tricalcium phosphate with sulphur, and pot and field trial are being conducted in Senegal. The effects of soil humidity, the addition of calcium carbonate and the source of phosphate on solubilization as measured in terms of pH and bicarbonate extractable were investigated. It was found that sulphur effectively solubilized the tricalcium phosphate, while

increased soil humidity strongly enhanced solubilization.

In Australia, Mrs. Joan Ragasch of the CSIRO Soils Division, granulated powdered sulphur and rock phosphate by mixing with a small volume of water in a rotating horizontal drum to give granules of optimum size and porosity for colonization by micro-organisms. After inoculation with soil rich in sulphur oxidizing organisms, these granules were examined for rate and amount of sulphur oxidation, release of water-soluble phosphate and changes in pH and titration acidity by the use of both continuous and intermittent aerobic perfusion technique. In the field and pot trials, the plants grown with rock phosphate-sulphur were intermediate between that obtained from rock phosphate alone and from superphosphate, when these were applied at equivalent rates of phosphorus. In a second year residual trial, the rock-phosphate-sulphur was as good as superphosphate and better than rock phosphate.

[World Crops, 15 (1963), 326-327]

### Slurry Fertilizers

Most clear liquid fertilizers necessarily are of relatively low plant food content to avoid settling out of crystals, which would settle and cake in storage. But methods now have been developed for preventing settling, excessive growth and caking of crystals, so that products of high plant food content can be handled as liquid even though they contain large proportions of solids. TVA has developed several techniques for making such slurry or suspension fertilizers from wet process phosphoric acid.

When wet process phosphoric acid is ammoniated, impurities in the acid are precipitated which may settle and form a hard cake in the bottom of tanks. The precipitation of impurities may be prevented by adding a sequestrant, such as ammoniated superphosphoric acid. However, for a clear solution, the concentration of the product is limited by the solubility of the salts involved. If solubility is exceeded to obtain products of high plant food concentration, steps should be taken to prevent the crystals from growing to such a size that will cause plugging of application equipment, which can be done by adding a suspending agent. By adding 2 per cent clay to a 12-12-12 grade suspension made from ammonia, wet process acid, urea-ammonium nitrate solution and potassium chloride, there was no settling during 7 days of storage, no crystal

formation larger than 20 mesh and therefore sprayability was satisfactory.

In another study it was found that clay could be eliminated by use of a high pH and a low temperature neutralization method. A very stable 12-12-12 suspension was obtained by feeding acid and ammonia to a tank simultaneously with maintenance of pH at about 7.5-8.5.

There have been developments in the production of salt-suspension fertilizer from ammoniated superphosphoric acid base salt suspensions. One per cent addition by weight of clay is enough to keep the ammoniated superphosphoric acid salt combinations of 12-40-0 and 13-43-0 in suspension, and in fact 3 per cent addition is used so that there is adequate suspending agent present when the product is cold mixed with other materials to produce high analysis suspension fertilizers such as 15-15-15, 10-30-10 and 15-15-15.

TVA work has shown that it is now feasible to use triple superphosphate instead of phosphoric acid in the production of suspension fertilizers, which will be economically attractive in many areas.

Information is also being developed on the production of nitric phosphate suspension fertilizers from phosphate rock, nitric acid and ammonia, because such a process offers the ultimate in low cost of raw materials since the nitric acid serves the dual purpose of solubilizing the phosphate and of supplying part of the nitrogen in the product.

Considerable thought has been given to methods of incorporating secondary and trace elements in fertilizers so that the required amounts can be applied uniformly to the soil in an economical way.

[Chemical Fertilizer & Plant Food Industry, 108 (1964), 4, 26-27].

#### Automated Phosphate Granulated Plant

The largest and most versatile phosphate granulated plant in the U.S.A. has been placed in operation at the Bonnie phosphate chemicals complex of the International Minerals and Chemical Corpr. in Bartow (Florida). This new \$ 2,500,000 installation has a rated capacity of 250,000 tons of finished materials per year, and is designed to produce coarse and granular triple phosphate and diammonium phosphate. The new unit and the 200,000 tons/year diammonium phosphate plant completed two years ago are operated as a single unit with a common control. The new granulated superphosphates are much

improved in hardness and in uniformity of size and composition. A closed circuit television camera keeps an electronic eye on the granulation process.

Coarse and granular triple superphosphate are made by mixing steam, rock phosphate, 54 per cent phosphoric acid and run-of-pile triple superphosphate. To make diammonium phosphate, phosphoric acid and ammonia are mixed and piped to the granulator-ammoniator, where rock phosphate, phosphoric acid, ammonia, steam and water are added. The granulated triple superphosphate and diammonium phosphate then go to a 60 feet long dryer, where the moisture is driven off.

During production, tests are taken every hour at several stages of the process for the following analysis: screen size, total  $P_2O_5$ , APA, moisture and nitrogen. The company has completed a \$ 700,000 superphosphoric acid plant, which produces 71-72 per cent  $P_2O_5$ .

[Chem. Weekly, 9 (1964), 4, 14]

#### Fertilizer Granulating Plant

After having undergone successful trials in early 1964, the NKP granulating plant at Thana (near Bombay) of the Bharat Fertilizer Industries Ltd. commenced regular production at the beginning of June, 1964 and the plant has reached its licensed capacity of 40 tons/day of compound granulated fertilizer on a single-shift basis. The Company hopes to attain 33,000 tons per annum capacity per annum by the end of this year.

[Indian Press Serv., 14 (1964), 52, 3-4]

#### Fertilizer Units in Rajasthan

Sri Mohanlal Sukhadia, Chief Minister of Rajasthan, while presiding over the ninth meeting of the Rajasthan Mineral Advisory Board, said that the location of fertilizer factories might change according to the prospects of oil and gas in Jaisalmer area. The team of experts appointed earlier by the Government of India had approved Jai Samand in Udaipur, Kotah and Bikaner for the location of fertilizer factories.

[India Press Serv., 14 (1964), 52]

#### Farmer-Oriented Fertilizer Policy

A series of measures are proposed to be taken to make the fertilizer policy distinctly farmer-oriented during the Fourth plan. Towards this end, the distribution and price policies are currently being reviewed.

In the field of distribution, it is proposed to strengthen the co-operative machinery to ensure that the farmer gets adequate quantities of fertilizers at the right time and place. A proposal to set up a central marketing Corporation to streamline distribution arrangements is being examined. The Government is also understood to be keen on reducing fertilizer prices in order to ensure a favourable input-price ratio for the agriculturists.

A recent survey has shown that fertilizer consumption can be more than doubled if prices were cut adequately. The prices of urea and calcium ammonium nitrate have already been reduced by Rs. 100 and Rs. 32 per tonne respectively.

It has been decided that before the new types of fertilizers are put on sale, intensive propaganda among the farmers should be undertaken. Tentatively, the Fourth Plan target for fertilizer production is envisaged at 2 million tonnes in terms of nitrogen. The programme is to set up two additional plants every year with a capacity of over one lakh tons. In view of the shortfall in domestic production, the Government will seek large-scale imports of fertilizer from abroad.

[FAI Information Service, 5 (1964), 12, 4-5]

#### Fertilizer Plants in S. India

National Iranian Oil Co. is believed to have agreed to cooperate with the Indian Government in setting up a fertilizer plant in Madras and two fertilizer factories in Cochin. The plant in Madras will have a capacity of 0.80 to 1 lakh tonnes and will depend on imported ammonia. Iran which is surplus in ammonia is said to be keen to supply this commodity to India in exchange for iron ore and bauxite. The NICO representatives have suggested to Sri Humayun Kabir, Union Minister for Petroleum and Chemicals, that a team of engineers with members from each country might be appointed for a joint study of the various aspects of the production and consumption of ammonia and allied chemicals.

FAI Information Service, 5 (1964), 14, 6-7]

#### Technical Collaboration

Messrs Fertilizer & Chemicals (Travancore) Ltd. are negotiating with Davy Ashmore of U.K. for technical collaboration to manufacture fertilizer equipment in India. Talks are currently being held with regard to fabrication of complete

fertilizer plant and production of essential equipment and spares.

[Indian Chem. Engr., 5 (1963), 198]

#### **Fertilizer Plant in Kerala**

Sri O. V. Alagesan, Union Minister of State for Petroleum and Chemicals, said at Ernakulam on June 24 that a fertilizer plant and a petro-chemical industry are proposed to be set up as adjuncts to the public sector oil refinery in Cochin. A report on the fertilizer project was likely to be ready within a month.

[PTI, The Statesman, 26.6.64]

#### **Sulphuric Acid Plant at Sindri**

Sri O. V. Alagesan, Minister of State for Petroleum and Chemicals, said in the Lok Sabha on May 29 that Pyrites and Chemicals Development Co. Ltd., a Government of India undertaking, has planned to set up a 400 tons/day plant at Sindri for the production of sulphuric acid directly from pyrites, available at Amjhore, Bihar. [Chem. Weekly, 8 (1964), 52, 16]

The site for the sulphuric acid factory has already been selected, and the plant is likely to be commissioned early in 1966. It is expected to meet partially the requirements of Sindri fertilizers factory and the Bihar State superphosphate works.

#### **Price of Naphtha**

The ex-refinery price of raw naphtha, an important raw for synthesis gas manufacture, is to be fixed at Rs. 83.50 per tonne, exclusive of duties and other levies. A substantial portion of surplus naphtha from the private sector refineries is at present being exported, the export figure for 1963 being 365,000 tonnes. According to an expert team the net surplus of naphtha will reach the maximum in 1966, which is likely to be of the order of 1.1 million tonnes. In later years, this surplus will gradually come down to 800,000 tonnes on account of off-take by the new fertilizers and petro-chemical units. In future, the team suggests that refineries and naphtha-consuming industries should be built simultaneously.

[FAI Information Service, 5 (1964), 10, 6]

#### *Miscellaneous*

##### **Committees/Meetings**

1. Dr. S. P. Dhua, Asst. Technologist, P. & D. Division, attended the third meeting of the Maharashtra State Fertilizer Advisory Committee held in Bombay on June 17, 1964. Of the four suggestions put forward by him for discussion, the following two were accepted and therefore included in the agenda of the meeting: (1) sale promotion with reference to the products of new fertilizer factories,

(2) fertilizer needs of irrigated and non-irrigated areas in Maharashtra.

On the first item, it was concluded that apart from price incentives it is necessary to carry out field trials exclusively for nitrophosphate. While the State Government wanted the cost of the field trials to be borne entirely by the FCI Ltd. Trombay, it was felt that both planning and execution of the field trials will be too expensive. Therefore the F.C.I. should do the planning, design and supervision, and the State Government to conduct the trials in the cultivators' fields. For demonstrating the efficiency of nitrophosphates under soil conditions in Maharashtra, it is worthwhile establishing a fertilizers trial station somewhere in the State.

2. Sri A. K. Roy, Deputy Superintendent, P. & D. Division, attended the annual general as well as the Sectional Committee meetings of the Corrosion Advisory Bureau Metals Committee of the CSIR held on July 20 to 21, 1964 at Bangalore.

##### **Membership**

Sri M. S. Deo, Asst. Librarian, and Sri S. N. Roye, Technologist (Technical Publications Officer), of P. & D. Division have been admitted as Member and Associate Member respectively of the Indian Association of Special Libraries and Information Centres (IASLIC), Calcutta.

# STATISTICS

TABLE 1—FERTILIZER CONSUMPTION IN RELATION TO ARABLE LAND AND TOTAL POPULATION (METRIC TONS)

			Average Consumption per 1000 ha of Arable Land. <sup>1</sup>						
Countries			1949-50			1960-61			Population Factor <sup>2</sup> 1960
			N	P <sub>2</sub> O <sub>5</sub> <sup>3</sup>	K <sub>2</sub> O	N	P <sub>2</sub> O <sub>5</sub> <sup>3</sup>	K <sub>2</sub> O	
Western Europe	..	..	13.80	21.23	17.22	30.72	33.94	32.23	3.1
Austria	..	..	9.59	18.20	13.43	26.60	50.20	49.30	*4.0
Belgium	..	..	78.34	90.00	93.08	105.90	93.70	160.71	9.7
Denmark	..	..	22.19	30.43	31.31	44.53	41.67	64.88	1.6
Finland	..	..	5.41	22.44	10.09	24.14	39.53	28.94	1.7
France	..	..	*10.65	*17.51	16.78	26.39	40.99	35.03	2.1
Germany, Fed. Rep.	..	..	37.87	38.84	68.14	72.34	76.25	117.66	6.5
Greece	..	..	*7.59	*7.59	*1.52	19.76	15.82	2.44	2.2
Ireland	..	..	4.09	23.68	6.33	18.05	57.95	48.75	2.1
Italy	..	..	7.78	16.06	1.04	21.01	23.93	6.55	3.1
Luxembourg	..	..	39.60	67.81	44.65	62.65	81.51	79.62	4.1
Netherlands	..	..	131.24	114.57	140.24	215.21	107.89	133.01	11.0
Norway	..	..	45.40	45.60	61.83	59.36	55.33	63.63	4.2
Spain	..	..	2.01	6.60	*1.83	13.41	13.61	4.63	1.5
Sweden	..	..	15.91	26.37	14.29	29.50	28.78	23.20	2.1
Switzerland	..	..	16.46	62.37	27.20	36.92 <sup>4</sup>	98.17 <sup>4</sup>	95.89 <sup>4</sup>	12.2
United Kingdom	..	..	28.14	55.58	32.15	62.90	57.22	60.04	7.2
Yugoslavia	..	..	0.93	1.16	0.25	9.94	6.42	11.61	*2.2
Eastern Europe and U.S.S.R.	..	..	2.43	2.65	3.67	6.13	5.91	6.65	1.2
Bulgaria	..	..	—	—	—	21.75	10.81	1.28	1.7
Czechoslovakia	..	..	7.67	10.00	11.41	26.93	29.29	35.19	2.5
Germany, Eastern	..	..	36.44	18.72	67.00	48.44	44.38	98.76	3.4
Hungary	..	..	—	—	—	14.31	11.94	2.43	1.8
Poland	..	..	5.57	6.1	9.88	16.89	12.90	19.19	1.8
U.S.S.R.	..	..	*1.36 <sup>6</sup>	*1.9 <sup>6</sup>	*1.88 <sup>6</sup>	3.36 <sup>7</sup>	3.60 <sup>7</sup>	3.35 <sup>7</sup>	0.9 <sup>7</sup>
North America	..	..	4.39	8.96	4.89	12.57	11.37	9.16	0.9
Canada	..	..	0.86	3.11	1.55	2.16	4.04	2.38	0.4
United States <sup>8</sup>	..	..	5.06	10.12	5.52	14.82	12.94	10.61	1.0
Latin America	..	..	1.07	1.19	0.48	4.08	*2.62	2.33	2.0
Brazil <sup>9</sup>	..	..	*0.52	*1.31	*0.42	3.38	3.96	5.56	3.4
Chile	..	..	1.21	2.61	0.28	*4.53	5.37 <sup>10</sup>	2.94 <sup>10</sup>	1.3
Cuba <sup>11</sup>	..	..	8.09	5.18	5.79	13.24 <sup>10</sup>	9.93 <sup>12</sup>	11.28 <sup>10</sup>	3.5
Dominican Rep. <sup>13</sup>	..	..	1.76	*0.59	0.04	6.61 <sup>10</sup>	1.67 <sup>10</sup>	4.54 <sup>10</sup>	4.4
Mexico <sup>13</sup>	..	..	0.17	0.22	0.04	6.77	2.14	0.45	1.7
Peru	..	..	22.19	13.93	3.67	21.61 <sup>14</sup>	11.24 <sup>14</sup>	2.97 <sup>14</sup>	5.6

*Average Consumption per 1000 ha of Arable Land<sup>1</sup>*

<i>Countries</i>				1949-50			1960-61			<i>Population Factor<sup>2</sup></i> 1960
				<i>N</i>	<i>P<sub>2</sub>O<sub>5</sub><sup>3</sup></i>	<i>K<sub>2</sub>O</i>	<i>N</i>	<i>P<sub>2</sub>O<sub>5</sub><sup>3</sup></i>	<i>K<sub>2</sub>O</i>	
Near East	..	..	..	2.44	0.67	0.05	3.46	1.15	0.13	1.7
Israel	..	..	..	—	—	—	45.62	29.47	5.42	5.1
Turkey	..	..	..	*0.22	*0.05	*0.07	0.98	0.48	—	1.1
United Arab Rep.	..	..	..	38.04	5.73	—	71.19 <sup>7</sup>	14.49 <sup>7</sup>	1.31 <sup>7</sup>	10.5 <sup>7</sup>
Far East (excl. Mainland China & North Korea)	..	..	..	2.62	1.50	0.65	6.05	2.70	2.89	3.4
Ceylon	..	..	..	8.50	0.67	6.13	19.45 <sup>15</sup>	1.67 <sup>15</sup>	18.04	6.4 <sup>15</sup>
China; Taiwan	..	..	..	49.73	13.00	0.48	120.08	42.06	41.67	12.2
India	..	..	..	0.52	0.06	—	1.76	0.36	0.18	2.7
Indonesia	..	..	..	1.13	0.12	0.20	—	—	—	—
Japan	..	..	..	50.58	38.32	20.03	124.03	80.88	98.77	15.3
Korea, Rep. of	..	..	..	50.59	27.30	2.22	104.69	26.45	3.38	11.8
Philippines	..	..	..	*1.71	—	—	6.30	3.33	2.85	*4.1
Africa	..	..	..	0.16	0.71	0.16	0.58	0.97	0.40	1.0
Algeria	..	..	..	—	—	—	2.35	3.52	2.29	1.6
South Africa	..	..	..	1.48	14.75	0.98	5.30 <sup>16</sup>	12.36 <sup>16</sup>	3.25 <sup>16</sup>	1.5
Oceania	..	..	..	1.05	25.26	0.53	1.07	28.57	3.57	0.6
Australia	..	..	..	1.19	25.54	0.61	0.83 <sup>17</sup>	19.23 <sup>17</sup>	1.12 <sup>17</sup>	0.3 <sup>17</sup>
New Zealand	..	..	..	2.87	147.95	4.41	12.79 <sup>18</sup>	349.19 <sup>18</sup>	94.88 <sup>18</sup>	3.7 <sup>18</sup>
World Total (excl. Mainland China & North Korea)	..	..	..	3.34	5.19	3.52	7.86	7.55	6.55	1.8

\* Estimate

1. Data on arable land and land under permanent crops have been taken from FAO's Production Year-book, Table 1: Land Use. Arable land includes land planted to crops (double-cropped area counted only once), land temporarily fallow, temporary meadows for mowing or pasture, garden land and land under fruit trees, vines and fruit-bearing shrubs.
2. Number of total population per hectare of arable land.
3. Data exclude ground rock phosphate.
4. Arable land excludes land under tree crops.
5. Includes ground rock phosphate.
6. Consumption refers to 1960.
7. Area of arable land refers to 1961.

8. Includes Hawaii and Puerto Rico.
9. Arable land refers to land in agricultural holdings as per 1950 agriculture census.
10. Consumption refers to 1959/60.
11. Area of arable land refers to 1946.
12. Consumption refers to 1957/58.
13. Area of arable land refers to 1950 agriculture census.
14. Consumption refers to 1961/62.
15. Area refers to arable land plus permanent meadows and pastures.
16. Arable land includes area of wattle plantations.
17. Arable land includes cultivated grassland.
18. Arable land refers to agricultural holdings exceeding 10 acres (4.047 hectares) and suited outside of boroughs.

[The State of Food & Agriculture 1963, F.A.O., Rome (1963)]

TABLE 2—WORLD CONSUMPTION OF POTASH FERTILIZERS, (THOUSAND METRIC TONS K<sub>2</sub>O)

			1949-59	1952-53	1955-56	1959-60	1960-61	1961-62
<i>Western Europe</i>								
Austria	..	..	24.7	28.0	43.5	84.0	86.5	99.0
Belgium	..	..	93.1	132.0	148.5	155.5	152.2	152.7
Denmark (1)	..	..	84.1	153.4	157.1	179.4	180.6	179.2
Finland	..	..	24.9	47.1	55.5	71.3	77.2	76.2
France (2)	..	..	354.5	370.6	581.3	685.9	749.9	—
Germany, Fed. Rep.	..	..	589.5	770.8	847.0	1046.6	1005.9	1036.1
Greece	..	..	*5.0	3.3	3.8	7.1	9.0	9.8
Iceland	..	..	*0.9	1.3	1.8	2.1	1.8	2.5
Ireland	..	..	9.5	24.2	37.6	58.0	66.4	79.2
Italy	..	..	16.0	34.9	57.0	108.2	103.8	127.5
Luxembourg	..	..	3.8	4.8	5.4	6.2	6.1	5.8
Netherlands	..	..	153.0	157.9	165.4	152.6	138.2	126.3
Norway	..	..	50.2	47.6	48.7	55.0	53.7	52.8
Portugal (3)	..	..	*4.0	3.1	6.1	10.5	6.9	10.4
Spain	..	..	*35.0	46.5	82.4	76.0	95.0	—
Sweden (4)	..	..	53.6	67.8	86.9	86.2	83.5	85.5
Switzerland	..	..	13.3	19.0	22.0	40.0	42.0	44.0
United Kingdom	..	..	239.0	235.0	311.0	434.0	438.6	—
Yugoslavia (3)	..	..	2.0	4.6	—	101.2	96.1	61.4
Total	..	..	1,760.0	2,150.0	2,690.0	3,360.0	3,400.0	3,500.0
<i>Eastern Europe and U.S.S.R.</i>								
Bulgaria (3)	..	..	—	—	0.6	2.5	5.9	—
Czechoslovakia	..	..	62.9	111.4	149.1	215.4	191.0	—
Germany, Eastern	..	..	339.0	411.0	457.9	499.4	500.7	—
Hungary	..	..	—	—	—	20.6	(5) 13.8	(6) 23.2
Poland	..	..	166.2	205.7	273.7	312.9	311.4	—
Rumania (3)	..	..	—	—	—	1.1	4.0	12.0
U.S.S.R. (3)	..	..	(7) 422.0	(8) 519.0	728.0	787.0	766.0	703.0
Total	..	..	1,000.0	1,260.0	1,630.0	1,840.0	1,790.0	*1,780.0
<i>North America</i>								
Canada	..	..	56.4	71.0	106.1	84.9	99.6	—
United States (9)	..	..	1020.0	1578.0	1700.7	1953.4	1967.2	2,013.9
Total	..	..	1,080.0	1,650.0	1,810.0	2,040.0	2,070.0	2,120.0

				1949-59	1952-57	1955-56	1959-60	1960-61	1961-62
<i>Latin America</i>									
Argentina	..	..	..	*1.6	*1.6	3.2	—	—	—
Barbados	..	..	..	2.4	1.2	2.7	2.6	2.8	2.6
Brazil (3)	..	..	..	*8.0	*16.0	41.6 <sup>10</sup>	57.4	106.2	—
British Guiana	..	..	..	—	0.1	1.2	2.9	1.4	2.2
Chile	..	..	..	1.6	3.6	6.0	16.2	—	—
Columbia	..	..	..	*3.0	8.0	12.4	—	—	—
Costa Rica (3)	..	..	..	—	—	—	5.0 <sup>11</sup>	—	—
Cuba	..	..	..	11.4	6.5 <sup>12</sup>	—	22.2	—	—
Dominican Republic	..	..	..	—	*0.7	1.5 <sup>13</sup>	3.1	—	4.2
Ecuador	..	..	..	0.1	—	2.0	1.5	3.9	—
El Salvador	..	..	..	*0.2	—	4.0	—	4.8	—
Guadeloupe	..	..	..	*—	1.4	—	7.8	—	—
Guatemala	..	..	..	*0.5	—	0.6	2.0	3.1	2.1
Jamaica (3)	..	..	..	0.8	1.8	3.3 <sup>10</sup>	5.4	5.0	5.5
Martinique (3)	..	..	..	—	2.9	5.7 <sup>10</sup>	*5.7	—	—
Mexico	..	..	..	0.8	2.4	5.5	*6.0	*9.0	—
Peru	..	..	..	6.0	2.4	6.0	*3.3	—	5.8
Trinidad and Tobago	..	..	..	0.8	0.9	1.3	2.0	2.7	1.9
Uruguay	..	..	..	—	0.5	—	9.2	—	—
Venezuela	..	..	..	*0.6	*1.0	4.0	4.0	3.7	—
Total	..	..	..	40.0	50.0	120.0	180.0	*240.0	*250.0
<i>Near East</i>									
Cyprus	..	..	..	0.2	—	0.3	0.7	0.6	0.7
Iran	..	..	..	—	—	0.1	1.0	1.5	—
Israel	..	..	..	—	1.1	2.8	2.1	2.2	2.3
Lebanon	..	..	..	*1.3	1.6	1.4	1.7	2.8	3.0
Lybia (Tripolitania)	..	..	..	—	—	0.5 <sup>15</sup>	0.3 <sup>14</sup>	—	—
Syria	..	..	..	—	0.1	0.1	0.1	0.5	—
Turkey	..	..	..	*1.0	2.5	6.3	4.8	0.1	0.1
United Arab Republic (3)	..	..	..	—	0.1	0.1	—	3.2	—
Total	..	..	..	—	10.0	10.0	10.0	10.0	10.0
<i>Far East</i>									
Ceylon	..	..	..	9.0	9.2	22.9	25.4	27.7	30.3
China: Taiwan	..	..	..	0.4	14.1	17.9	26.5	36.2	33.4
Fed. of Malaya	..	..	..	0.8	0.8	3.8	8.8	9.7	10.0
India	..	..	..	—	3.0	6.7	31.9	28.9	—
Indonesia	..	..	..	2.2	0.4	2.7	6.2	10.4	—
Japan	..	..	..	120.0 <sup>16</sup>	210.0 <sup>18</sup>	385.9	524.7	599.7	492.8
Korea, Rep. of	..	..	..	4.3	7.0	.8.8	6.0	7.1	17.1
North Borneo	..	..	..	—	0.1	—	0.4	0.3	0.2
Pakistan	..	..	..	—	—	0.1	0.2	9.0	6.0
Philippines	..	..	..	—	5.0	4.4	—	19.3	31.1
Ryukyu Islands	..	..	..	—	—	0.9	2.3	3.9	—
Singapore	..	..	..	—	—	—	2.4	2.1	—
Thailand	..	..	..	—	—	—	2.4	2.1	—
Viet-Nam, Rep. of	..	..	..	0.7 <sup>17</sup>	—	1.0	4.2	3.5	4.8
Total	..	..	..	140.0	250.0	460.0	650.0	760.0	680.0

				1949-59	1952-57	1955-56	1959-60	1960-61	1961-62
<i>Africa</i>									
Algeria	..	..	..	—	9.1	8.8	16.8	16.2 <sup>4</sup>	—
Cameroon	..	..	..	—	0.2	0.7	1.1	1.4	—
Kenya (3)	..	..	..	—	0.1	0.4	0.2	1.1	—
Madagascar	..	..	..	—	0.3	0.4	0.7	0.7	—
Mauritius	..	..	..	2.2	2.8	3.1	5.2	5.6	5.0
Morocco (3)	..	..	..	—	4.4 <sup>18</sup>	6.1 <sup>18</sup>	5.2	6.3	5.8
Mozambique (3)	..	..	..	—	—	—	0.3	—	—
Nigeria	..	..	..	—	0.2	0.8	0.9	1.7	0.8
Reunion	..	..	..	—	1.2	1.5	1.7	2.0	2.9
Rhodesia-Nyasaland	..	..	..	0.3	*7.9	9.2	12.1	17.9	15.0
South Africa	..	..	..	6.0	8.6	26.8	32.9	33.4	39.0
Spanish Equatorial Region	..	..	..	—	—	—	0.3	—	—
Swaziland	..	..	..	—	0.1	0.1	1.3	1.4	—
Tanganyika (3)	..	..	..	0.3	0.1	—	0.5	0.5	0.5
Tunisia	..	..	..	0.4	0.2	1.3	2.2	—	—
Uganda (3)	..	..	..	—	—	—	0.5	0.3	—
Total	..	..	..	*30.0	40.0	60.0	80.0	90.0	*90.0
<i>Oceania</i>									
Australia	..	..	..	7.8	8.6	23.3	22.5	33.2	47.4
New Zealand	..	..	..	4.3	10.8	21.2	47.5	61.0	74.0
Total	..	..	..	10.0	20.0	40.0	70.0	100.0	120.0
World Total	..	..	..	4,000.0	5,400.0	6,800.0	8,200.0	8,500.0	8,600.0

\* Estimate

1. Fertilizer Year : August-July.
2. Fertilizer Year : May-April
3. Calendar Year referring to the first part of the split year.
4. Fertilizer Year : June-May
5. 1960.
6. 1961.
7. 1950.
8. 1953.

9. Includes Hawaii and Puerto Rico.
10. 1956.
11. 1958.
12. 1953/54.
13. 1955.
14. 1958/59.
15. 1956/57.
16. Includes Ryukyu Islands.
17. 1950/51.
18. Former French zone only

[The State of Food & Agriculture, F.A.O., Rome (1963)]

TABLE 3—WHOLESALE PRICES OF FERTILIZERS

Year	Ammonium Sulphate			Ammonium Nitrate			Superphosphate			Potassium Chloride			Potassium Sulphate					
	West Germany, DM, 100 Kg.	Japan, 1000 yen, 100 Kg.	U.K., £/ton	U.S.A., \$/2000 lbs.	France, New Franc/ 100 Kg.	West Germany, DM, 100 Kg.	U.K., £/ton	U.S.A., \$/2000 lbs.	France, New Franc/ 100 Kg.	Italy, 1000 lira/ Kg.	West Germany, DM, 100 Kg.	U.S.A., \$/ 2000 lbs.	France, New Franc/ 100 Kg.	West Germany, New Franc/ DM, 100 Kg.				
1956	22.9	2.14	20.9	35.3	31.9	23.2	17.8	64.6	10.4	13.10	1.65	15.1	17.6	16.6	11.5	22.8	237	18.7
1957	22.9	2.08	21.3	32.0	32.0	23.8	18.2	64.0	10.4	14.86	1.67	15.3	17.9	16.3	11.5	21.6	233	18.7
1958	24.1	2.01	21.5	32.0	34.2	24.4	18.5	68.2	12.2	14.86	1.67	15.2	18.0	18.3	11.7	20.5	238	18.7
1959	24.1	1.93	20.8	32.0	36.9	24.4	18.5	66.8	11.6	14.86	1.62	14.4	18.0	19.3	12.0	20.8	255	18.7
1960	23.6	2.09	20.6	32.0	37.2	23.4	18.5	67.1	11.7	14.86	—	14.1	18.0	20.2	12.1	21.8	261	18.7
1961	23.1	2.02	20.2	32.0	37.3	22.1	17.4	66.5	11.7	14.86	1.84	13.6	18.0	20.9	12.1	23.2	270	18.7

[Production Year-Book 1962, F.A.O., Rome (1963)].

TABLE 4—PERCENTAGE INCREASE IN PRODUCTION AND CONSUMPTION OF N, P<sub>2</sub>O<sub>5</sub> AND K<sub>2</sub>O IN INDIA

Particulars	Percentage increase from			
	1959-60	1960-61	1961-62	1959-60
	to 1960-61	to 1961-62	to 1962-63	to 1962-63
<i>Production</i>				
Nitrogen (N)	33.9	37.7	32.9	145.1
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> )	4.5	21.7	54.5	96.5
N+P <sub>2</sub> O <sub>5</sub>	22.7	32.5	39.4	126.6
<i>Consumption</i>				
Nitrogen (N)	6.1	51.0	21.7	95.0
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> )	7.1	17.3	62.4	103.9
Potash (K <sub>2</sub> O)	64.4	12.0	78.4	157.7
N+P <sub>2</sub> O <sub>5</sub> +K <sub>2</sub> O	10.4	38.9	31.0	100.9

Note: Figures for phosphoric acid do not include ground rock phosphate used directly or bonemeal.

[Production and Consumption of Fertilizers—Annual Rev. 1962-63, Fertilizer Assn. of India, New Delhi (May 1963)]

TABLE 5—PROPORTION OF PRODUCTION AND CONSUMPTION OF FERTILIZERS BY DIFFERENT REGIONS IN INDIA IN 1961-62

Region	Percentage of production and consumption						
	Production			Consumption			
	N	P <sub>2</sub> O <sub>5</sub>	N+P <sub>2</sub> O <sub>5</sub>	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	N+P <sub>2</sub> O <sub>5</sub> + K <sub>2</sub> O
South	7.5	54.8	21.6	47.4	50.3	70.7	49.3
West	2.3	26.5	9.5	18.6	25.5	9.2	18.9
North	32.1	4.7	23.9	16.7	3.8	0.1	13.8
East	58.1	14.0	45.0	17.1	12.9	20.0	16.8
Other users	—	—	—	0.2	7.5	—	1.2

Note: Consumption percentages take into consideration the imported fertiliser materials also.

[Production and Consumption of Fertilizers—Annual Rev. 1962-63, Fertilizer Assn. of India, New Delhi (May 1963)]

TABLE 6—PRODUCTION OF NITROGEN IN DIFFERENT REGIONS OF INDIA

Region			Production of nitrogen (N) (metric tonnes)				Percentage increase from			
			1959-60	1960-61	1961-62	1962-63*	1959-60 to 1960-61	1960-61 to 1961-62	1961-62 to 1962-63	1959-60 to 1962-63
South	..	..	8,396 (10.1)	10,703 (9.6)	11,567 (7.5)	17,535 (8.6)	27.5	8.1	51.6	108.8
West	..	..	1,141 (1.4)	2,416 (2.2)	3,547 (2.3)	3,895 (1.9)	111.7	46.8	9.8	241.4
North	..	..	849 (1.0)	13,054 (11.7)	49,262 (32.1)	65,435 (32.0)	1,437.6	277.4	32.8	7,607.3
East	..	..	72,928 (87.5)	85,373 (76.5)	89,259 (58.1)	117,353 (57.5)	17.1	4.6	31.5	60.9
India	..	..	83,314 (100.0)	111,546 (100.0)	153,635 (100.0)	204,218 (100.0)	33.9	37.7	32.9	145.1

Note: Figures in brackets denote the proportion of production in each region to the total all-India figure.

\*Estimated.

[Production and Consumption of Fertilizers—Annual Rev. 1962-63, Fertilizer Assn. of India, New Delhi (May 1963)]

TABLE 7—PRODUCTION OF PHOSPHORIC ACID IN DIFFERENT REGIONS OF INDIA

Region			Production of phosphoric acid ( $P_2O_5$ ) (metric tonnes)				Percentage increase from			
			1959-60	1960-61	1961-62	1962-63*	1959-60 to 1960-61	1960-61 to 1961-62	1961-62 to 1962-63	1959-60 to 1962-63
South	..	..	22,870 (44.5)	30,057 (56.0)	35,795 (54.8)	53,329 (52.8)	31.4	19.1	49.0	133.2
West	..	..	14,368 (27.9)	14,398 (26.8)	17,355 (26.5)	26,288 (26.0)	0.2	20.5	51.5	83.0
North	..	..	6,956 (13.5)	2,334 (4.3)	3,049 (4.7)	7,196 (7.1)	-66.4	30.6	136.0	3.5
East	..	..	7,213 (14.1)	6,933 (12.9)	9,161 (14.0)	14,181 (14.1)	-3.9	32.1	54.8	96.6
India	..	..	51,407 (100.0)	53,722 (100.0)	65,360 (100.0)	100,994 (100.0)	4.5	21.7	54.5	96.5

Note: Figures in brackets denote the proportion of production in each region to the total all-India figure.

\*Estimated.

[Production and Consumption of Fertilizers—Annual Rev. 1962-63, Fertilizer Assn. of India, New Delhi (May 1963)]

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The opinions expressed by the authors are their own and do not necessarily reflect the views of the Planning and Development Division of the Fertilizer Corporation of India Ltd.



The Main Building of the Planning and Development Division of FCI Ltd. at Sindri.

# Slagging Gas Generator Pilot Plant

By

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Several processes have been developed on the manufacture of synthesis gas—a basic raw material for the production of fertilizers, methanol, synthetic fuels, etc.—from solid fuels including high ash, non-coking coal. Slagging gasification is a process for gasifying lump coke in a fixed bed and removing the ash in a molten state. A pilot gas generator has been designed and put into commission by this Division at Sindri; The different aspects of the design and developmental work on this plant and the operational data obtained during its trial runs have been described.

## Introduction

During the past quarter of this century there have been considerable developments in the manufacture of synthesis gas—the basic raw material for fertilizers, synthetic liquid fuels, etc. Among the processes developed for gasification of solid fuels, the following may be mentioned: Winkler process, for the reactive fines in a boiling bed; Kopper-Totzek, for the pulverised coal in suspension; Lurgi for gasifying coal in a fixed bed at high pressure, and Slagging generator for gasifying lump coke in a fixed bed and removing ash as molten slag. The gasification process to be adopted must suit the fuel available, although some processes are a little more versatile than others. Even for similar fuels, the performance of a gasification unit varies depending on fuel characteristics, such as, ash content, ash fusion temperature, reactivity, etc.

At the Sindri Unit of F.C.I. Ltd., synthesis gas required for the manufacture of ammonia is obtained by gasification of sized coke in cyclic semi-water gas generators, which operate satisfactorily with sized coke having high ash fusion temperature. In order to conserve the coking coals for metallurgical use, coke prepared from Raniganj coals having lower ash fusion temperature was studied, which indicated that with such coke clinkering tendency increased affecting adversely the output of the generators.

Much work has been done on gasification of solid fuels under slagging condition in Belgium, E. & W. Germany and other Western countries. Though some data on the slagging gasification are available in literature, these are not directly applicable to Indian conditions as the fuel characteristics in this country vary

widely. It was, therefore, felt useful to design a slagging gas generator and study in it the gasification characteristics of high ash coke having low ash fusion temperature, so that the data could form the basis for designing an economical type of such generators.

The main advantages of the slagging gas generator<sup>1,2</sup> are: (i) the continuous nature of operation; (ii) the high capacity per unit area of the hearth; (iii) reactivity of the fuel does not play a significant role as the operating temperatures are high; (iv) and methane content in the outlet gas is relatively small.

Extensive studies have been carried out in this Division of the F.C.I. Ltd. on ash fusion properties of the different blended coke, the characteristics of refractories, slag flow characteristics, nozzle designs and other related problems. Based on these studies a pilot slagging gas generator has been designed, fabricated, installed and put into operation departmentally (Fig. 1).

## Operating Principles

The pilot generator gasifies high ash coke in a fixed bed with fuel and the reactant gases flowing counter-current.<sup>3,4</sup> The major advantages of the counter-current gasification are: (a) the sensible heat of the product gas is utilised for drying, devolatilisation and preheating of the down-coming fuel, and hence the thermal efficiency of the generator is increased; (b) there is enough excess carbon in the reaction zone for the endothermic reactions to proceed to completion, which makes the operation safer, (c) a high blast rate can be maintained causing the flow turbulent with large heat and mass transfer rate.



Fig. 1. General View of the Slagging Gas Generator Pilot Plant.

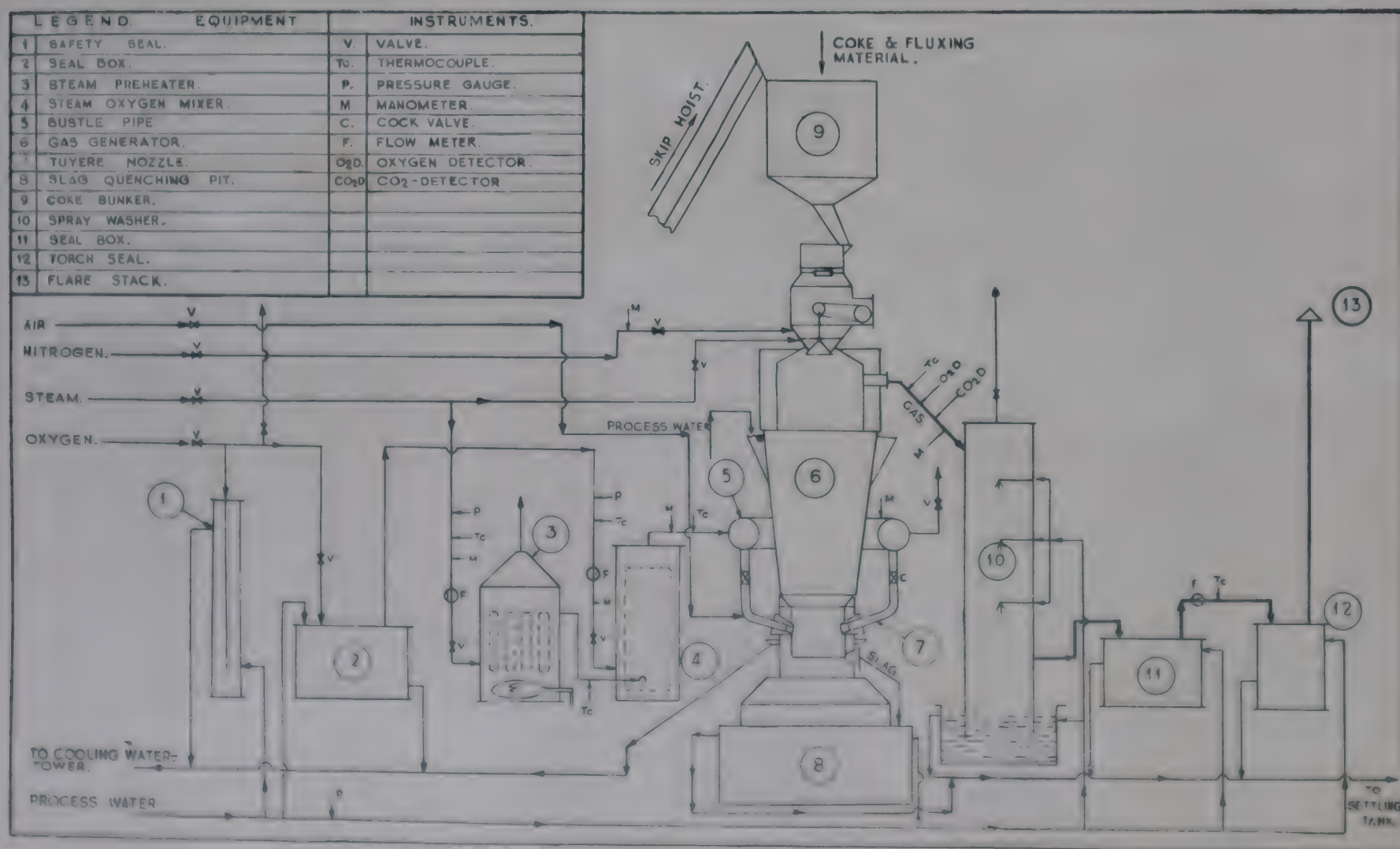


Fig. 2. Flow Diagram of the Slagging Gas Generator Pilot Plant.

In operating the plant, mixture of oxygen and pre-heated steam is admitted at the base of the fuel bed, of the generator, and thus a temperature sufficiently high to melt the ash is obtained. Since the blasts are introduced through the comparatively small cross sections of the tuyere nozzles, the reactions are completed at a rapid rate within a relatively short zone.

Operation under the slagging condition is simple because there are no moving parts like a rotating grate or any other mechanical device for removing ash. Ash is removed in the form of slag by tapping from the bottom of the hearth periodically. The operating conditions are maintained in such a manner that the slag has the proper fluidity for free flow. The flow properties of slag depend upon the hearth temperature and the ash fusion temperature, which depends on silica ratio of the ash\* and ash composition.

These characteristics can be improved upon by the addition of fluxing agents, like limestone, blast furnace slag, dolomite and iron oxide. The quantity and the type of flux added depend on the properties of the ash and the cost factor involved.

### Design of the Plant

The pilot slagging generator has been designed on the basis of the anticipated excess oxygen available from the existing air fractionation unit. The entire work on design, development and installation of the pilot plant was carried out in this Division, while some parts of the equipment were fabricated or purchased from outside (Fig. 2).

The unit has been designed with a maximum throughput of 50 tonnes/day of coke. The internal diameter of the generator at the tuyere is 1150 mm, and the height of the fuel bed above the tuyere is 3500 mm. (Fig. 3). Only one row of the six tuyere nozzles is installed at an inclination of 17° towards the centre of the hearth. The height of the nozzle mouth from the bottom of the generator is 600 mm., and the internal diameter of the nozzle is 50 mm. The nozzle has been fabricated entirely from an alloy steel. An arrangement for changing the internal diameter of the nozzle has been made with a copper ring so that the velocity of the blast can be varied in the range of 75-125 m/sec. The mouth and the holder of the nozzle are water-cooled. The entire block is fabricated in such a way that the whole assembly can be disconnected, removed even in hot condition, repaired and then replaced. To avoid the

sticking of the nozzle to the refractories or slag, the exterior of the nozzle is lubricated with a high temperature lubricant, e.g. molybdenum sulphide, before installation. The tuyere nozzles have a sight hole which is used for poking also. To overcome the tendency of condensate deposition in the sight glass air or nitrogen under pressure is introduced when observing through the sight glass.

There are two cinder notches, one of which is flush with the base of the hearth and the other installed at a height of 250 millimetres. The molten slag is normally tapped from the bottom cinder notch, having internal diameter of 63 mm. (Fig. 4). These notches, fabricated from boiler grade steel plate, have been tried successfully. The entire block of the cinder notch is water-cooled.

To select a suitable refractory for lining the hearth area, extensive bench-scale studies on the spalling properties of refractories and the nature of slag penetration into the refractory bricks at high temperature were carried out. A wide variety of refractory bricks, e.g. high heat-duty fire-bricks, bonded sillimanite, Alumo and silica bricks and natural sillimanite, have been tested, of which the natural sillimanite gave the best results. Even at 1500°C, practically there was no slag penetration with natural sillimanite. This refractory was resistant to spalling, and had low and regular coefficient of expansion and high mechanical strength. It was observed that at 1450°-1500°C, sillimanite gets practically transformed into the mullitic state having good resistance to heat and slag attack.

Hence the base of the generator and the hearth area are lined with natural sillimanite refractory blocks backed with high heat duty fire-bricks to resist the high temperature. The top portion of the generator and the crown and a portion of the raw gas exit pipe are also lined with high heat duty fire-bricks. The part of the generator between the bottom hearth and the top is bare metal, which is cooled by the trickling water down over the outside from a serrated cooling water distributor.

### Operation of the Plant

Before starting the plant, the refractory brick-lining of the generator was heated by burning coke oven gas to remove the moisture from the brick-work. After the heating-up, 30-50 mm. size wood charcoal was charged, and filled up to a certain height above the tuyere level. The charcoal was then ignited by a coke oven gas burner introduced through the cinder notch. A mixture of coke and admixture consisting of

\* Silica Ratio =  $\frac{\text{SiO}_2}{\text{SiO}_2 + \text{equivalent Fe}_2\text{O}_3 + \text{MgO} + \text{CaO}}$

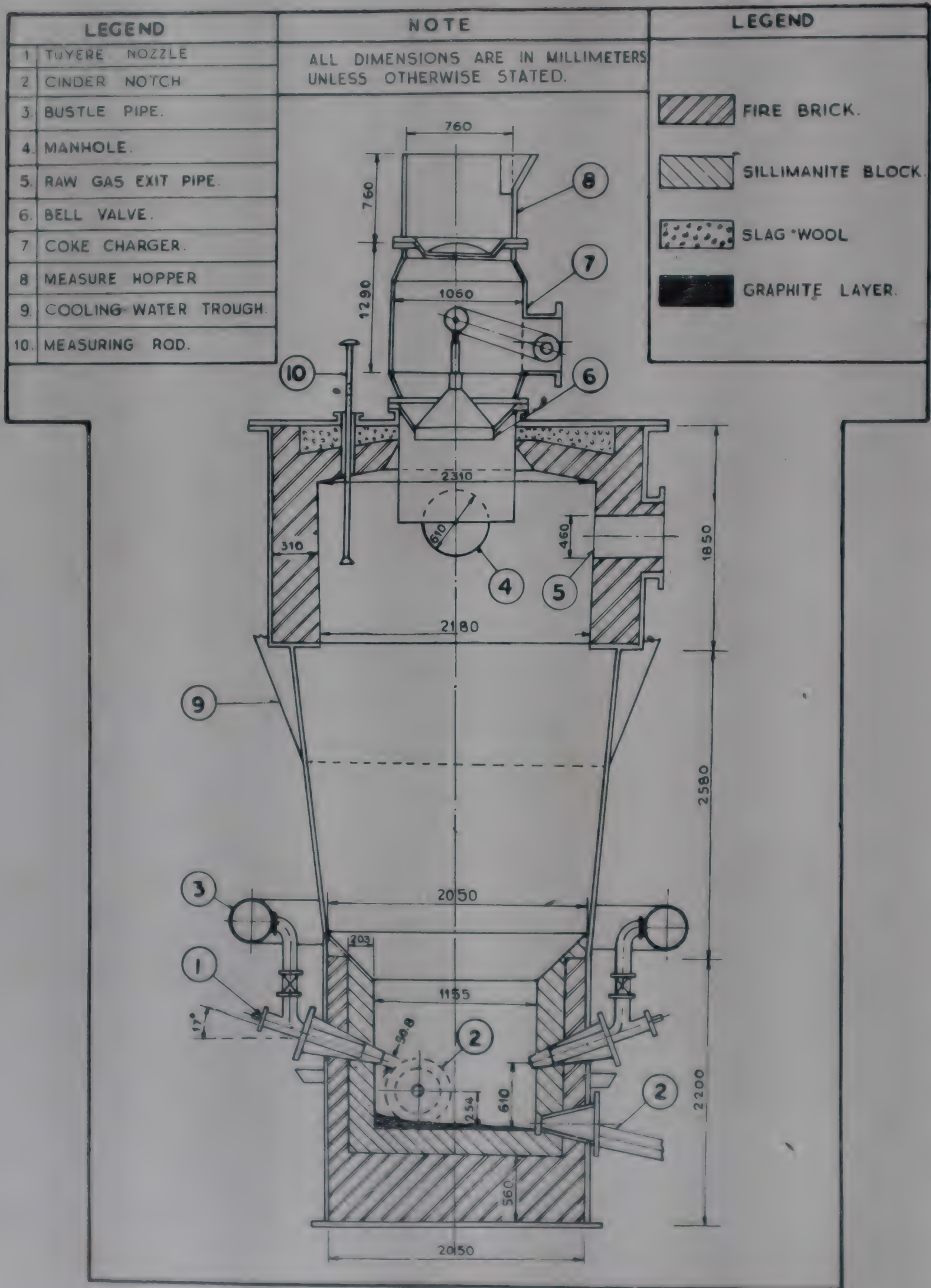


Fig. 3. Gas Generator.



Fig. 4. Slag Tapping Arrangement.

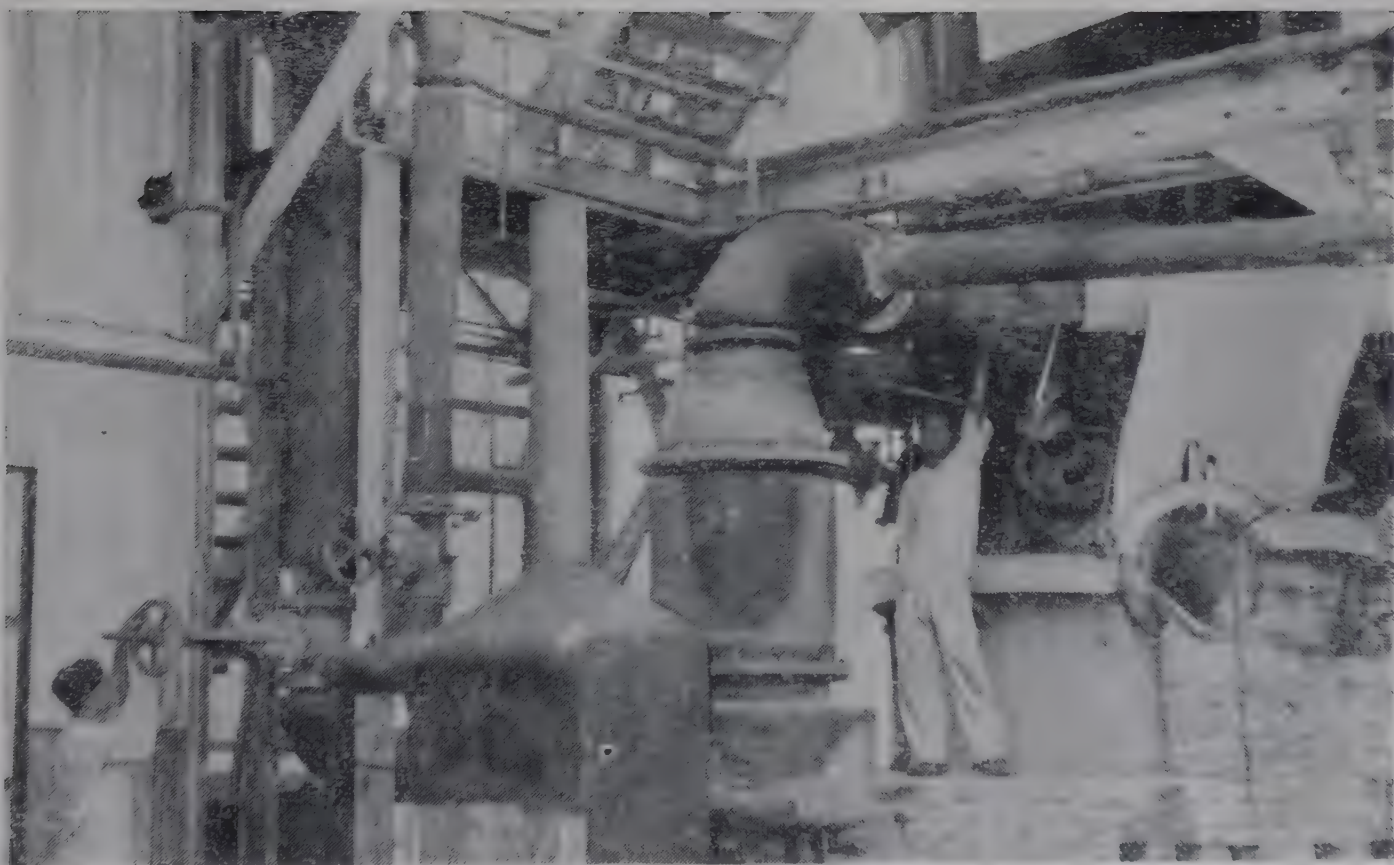


Fig. 5. A View of the Steam Preheater and Oxygen-Steam Mixer.

blast furnace slag and limestone was fed into the bunker at the top of the generator by means of an electrically operated skip hoist. From the bunker, the fuel and the admixture were taken into the measuring hopper and then fed into the generator through a Bell and cone feeding device. During charging the charger was purged with steam and nitrogen.

Oxygen and preheated steam in a preadjusted ratio were thoroughly mixed and then the blast of the mixture was allowed to enter the bustle pipe and vented through a vent on the bustle pipe (Fig. 5).

When the charcoal was found fully ignited, the coke oven gas burner was put off and taken out from the cinder notch. Both the cinder notches were plugged with iron plugs. The mixture of steam and oxygen was then introduced into the generator slowly and carefully by opening the plug cocks of the tuyere nozzles. The blast was gradually increased by closing the vent line of the bustle pipe.

The ignited fuel bed inside the generator was frequently observed through the sight glass and the height of the fuel bed was built up to desired level. The height of the fuel bed was measured by means of a dipstick from the top of the generator. At the time of starting, the stack at the top of dust scrubber was kept open. Initially, the gas was vented through the vent pipe at the top of the dust scrubber, but when the generator became steady the gas was taken through the dust scrubber where the gas was cleaned by water spray and after that it was taken through a water seal to the flare stack where it was burnt. The gas make was measured by means of an orifice meter.

2-3 hr after the start the molten slag gets accumulated at the bottom of the hearth, wherefrom it was tapped through the cinder notch (Fig. 4). The iron plug, meant for plugging the cinder notch, was taken out slowly, when the molten slag came out, which flowed through a channel covered with green sand, and was then taken to a quenching pit where the slag was quenched by pressure water from fish tail jets. Due to sudden quenching, the slag was granulated and then it was disposed off. During the tapping, it was observed that in some cases, the molten slag did not come out through the cinder notch by merely removing the iron plug. In such cases a small hole was made in the solid slag at the mouth of the cinder notch by poking with a rod. Sometimes when it was found difficult to pierce a hole in the slag by a poking rod, oxygen cutting of the solid slag was resorted to.

The temperature of the generator hearth, as measured by the optical pyrometer, was about 1700°C. The

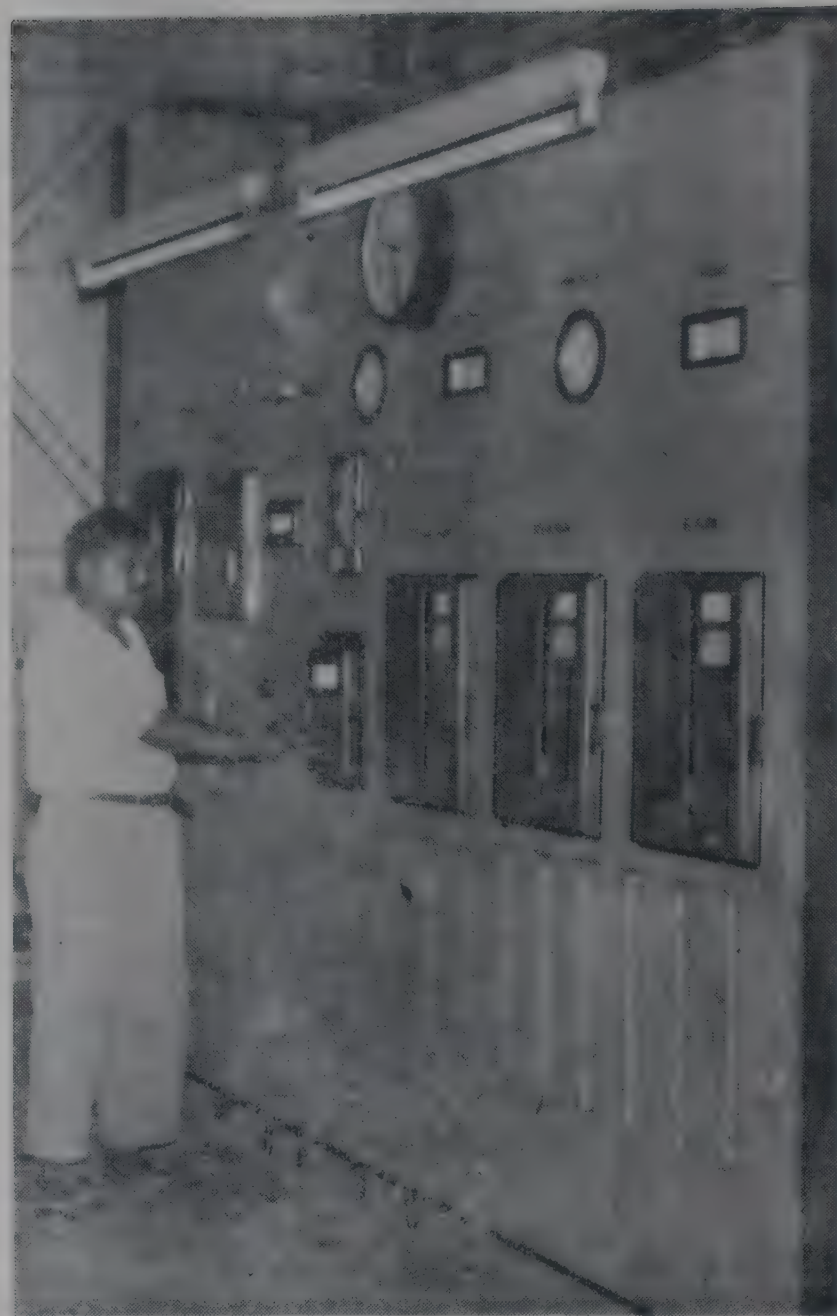


Fig. 6. Control Panel of the Pilot Plant. \

flow of oxygen and steam was measured by orifice flow meters. The temperatures at different points were measured and indicated or recorded according to necessity (Fig. 6). The percentages of carbon dioxide and free oxygen in the raw gas were detected by CO<sub>2</sub> mono-recorder and Magnos† respectively.

#### Operational Control and Safety Measures

*Steam-oxygen Ratio in Blast:* This blast was analysed periodically for oxygen content from which the ratio was obtained, although oxygen and steam flows were measured and the purity of oxygen was known.

*Preheat Temperature of Steam:* Steam was preheated in a gas fired preheater to have some superheat after the mixing of oxygen and steam, so that there

† a paramagnetic detection apparatus

would be no slag solidification at the tip of the tuyere nozzle.

*Generator Top Temperature:* This was regularly measured by a recorder, which indirectly furnishes information on fuel bed height and the regularity in charging, etc.

*Oxygen in Raw Gas:* Presence of free oxygen in the raw gas beyond certain limit leads to an explosion. With oxygen break through, the carbon dioxide content in the raw gas also increases. In view of the importance of carbon dioxide and oxygen in the gas, there are optical and acoustical signals for their indication, in addition to their measurement. When oxygen is found to be more than 1 per cent immediate corrective action is taken.

*Pressure Drop:* The differences of pressure between various points gave indication of channelling, slag depth, choking of the tuyere nozzles and lines, etc. The blast pressure at the nozzle was maintained between 900 to 1000 mm. of water.

*Safety Equipment:* Although the operational platforms were well ventilated, operators were provided with protective clothing and safety equipment.

*Cooling Water:* The generator shell, tuyere nozzles, nozzle holders, and cinder notches are water-cooled. There is an alarm for low water pressure. As an emergency measure, a water tank with circulating pump has been provided for supplying water under pressure.

*Banking the Generator:* In case of failure of power or any other supply for a short duration the generator can be banked. The following procedure is followed for banking the generator: (i) tap the slag before shut-down, (ii) open the vent line at the top of the dust scrubber; (iii) open the vent line of the blast and close the plug cocks of the tuyere nozzles; (iv) open some of the sight-holes of the tuyere nozzles; (v) and stop the charging of coke and admixture.

For a long shut-down, the following sequence should be adopted: (a) tap the slag completely; (b) open stack valve at the top of the dust scrubber; (c) after slag tapping, open the exhaust line of oxygen and stop slowly flow of oxygen; (d) continue steam flow into the generator for some time at a slow rate; and when the temperature has come down to 150°-160°C stop the steam flow; (e) pass nitrogen through the sight holes; (f) purge the generator with nitrogen till carbon monoxide in the exit gas comes down to the lower permissible limit; (g) keep the stack open, but the sight-hole lids of the tuyere nozzles and the plugs of the cinder

notches are to be kept closed; (h) and lastly, allow the generator to cool.

## Fuel, Fluxing Materials, Oxygen and Steam Used

For operating the plant, a mixture of 70 per cent coke and 30 per cent fluxing materials by weight was charged. Though a wide variety of non-caking fuels have been recommended during the trial runs sized hard coke was used. The coke was screened and its size was maintained in the range of 30-60 mm. (Table 2). Blast furnace slag and limestone were used as fluxing materials (Table 1). While the size of blast furnace slag was maintained within 20-50 mm. the same of limestone was in the range of 20-40 mm. (Table 2).

TABLE 1—COMPOSITIONS OF COKE, BLAST FURNACE SLAG, LIMESTONE, & SLAG FROM GAS GENERATOR

Material			Composition, %		
1. Coke	..	..	Ash	..	24.0
			Moisture	..	3.0
			V.M.	..	1.2
			Fixed carbon	..	71.8
2. Blast Furnace Slag	..	..	SiO <sub>2</sub>	..	25.9
			Al <sub>2</sub> O <sub>3</sub>	..	30.9
			CaO	..	38.8
			MgO	..	1.5
			Fe <sub>2</sub> O <sub>3</sub>	..	0.6
			S	..	0.7
			Loss on ignition	..	1.6
3. Limestone	..	..	SiO <sub>2</sub>	..	10.7
			Al <sub>2</sub> O <sub>3</sub>	..	2.1
			Fe <sub>2</sub> O <sub>3</sub>	..	0.6
			CaO	..	46.8
			SO <sub>3</sub>	..	0.3
			MgO	..	1.2
4. Slag Obtained from Slagging Gas Generator Pilot Plant	..	..	Loss on ignition	..	38.3
			SiO <sub>2</sub>	..	32.35
			Al <sub>2</sub> O <sub>3</sub>	..	27.30
			Fe <sub>2</sub> O <sub>3</sub>	..	1.20
			CaO	..	36.85
			MgO	..	2.00
			SO <sub>3</sub>	..	0.30
			Alkali	..	Nil

Extensive bench-scale experiments were carried out to determine the ratio of coke and fluxing agents so that the proper fluidity of the slag could be maintained during the operation of the plant. It was observed

TABLE 5—Contd.

HEAT BALANCE, DATUM TEMP.—0°C.

Run No. 2

Heat Input	KCal/hr
1. Heating value of Coke	71,22,000
2. Sensible heat of Coke	8,900
3. Sensible heat of Admixture	3,050
4. Enthalphy of steam introduced	2,24,500
5. Sensible heat of oxygen introduced.	18,100,
Total Heat Input .. ..	73,76,550

Heat Output	KCal/hr
1. Heating value of Raw Gas	55,80,500
2. Sensible Heat of Raw Gas	1,32,000
3. Sensible heat of molten Slag	2,05,000
4. Sensible heat of cooling Water	8,15,000
Total heat Output	67,32,500

$$\text{Thermal Efficiency of the Plant} = \frac{67,32,500}{73,76,550} \times 100$$

$$= 91.8\%$$

$$\text{Cold gas efficiency of the plant} = \frac{55,80,500}{73,76,550} \times 100$$

$$= 74.5\%$$

TABLE 6—OPERATIONAL DATA AT DIFFERENT COMMERCIAL &amp; PILOT PLANTS

Generator	SWG Plant at Sindri works	Slagging Generator pilot plant at Sindri	Slagging Generator at Leuna <sup>1,4</sup>
Internal diameter at hearth (grate), mm	3050	1150	2100
Fuel			
Kind of fuel	Coke. (size: 40 mm & larger).	Coke. (size: 40 mm—60 mm)	Coke. (size: 48 mm & larger).
Moisture of fuel, % wt.	4.0	3.2	1.8
Ash of fuel, % wt.	24.0	24.0	11.8
Ash Fusion temperature, °C	1430	1430	1300

## Output

Raw gas produced, Nm <sup>3</sup> /hour—	6,500	2,200	7,200
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## Composition of Gas:—

CO <sub>2</sub> — % Vol.	8.0	3.4	6.8
CO — „	31.3	65.4	61.4
H <sub>2</sub> — „	37.1	26.1	31.0
O <sub>2</sub> — „	Nil	0.36	Traces
CH <sub>4</sub> — „	0.6	0.44	„
CnH <sub>2n</sub> — „	Nil	Nil	Nil
Nitrogen— „	23.0	4.30	0.8

Gross heating value of gas, K. cal/M <sup>3</sup> at 15°C & 760 mm.	2082	2628	2651
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## Operation Characteristics

Operating temperature range at hearth/grate area, °C.	1200° to 850°	1650° to 1700°	1650° to 1700°
Raw gas exit temperature, °C.	500° to 600° (up run period) and 300° to 200° (down run period)	250	400

H <sub>2</sub> : CO Ratio in Gas	1.20	0.40	0.50
Coke consumption/1000 Nm <sup>3</sup> of Raw gas, Kg.	600	545	452
Oxygen consumption/1000 Nm <sup>3</sup> of Raw gas, Nm <sup>3</sup>	*1266 Nm <sup>3</sup> of air	245	242
Steam consumption/1000 Nm <sup>3</sup> of raw gas, Kg.	822	180	304
Oxygen requirement/1000 Nm <sup>3</sup> of CO & H <sub>2</sub> , Nm <sup>3</sup>	*1862 Nm <sup>3</sup> of air	264	262
Coke requirement/1000 Nm <sup>3</sup> of CO & H <sub>2</sub> , Kg.	770	590	490
Steam requirement/1000 Nm <sup>3</sup> of CO & H <sub>2</sub> , Kg.	1210	190	329
Raw gas produced/M. Tonne of Coke, Nm <sup>3</sup>	1918	1850	2212
Oxygen: steam Ratio in blast	—	66:34	53:47
Steam decomposition, %	35.0	88.7	90.1
Thermal efficiency, % (hot gas basis)	—	91.8	92.0

TABLE 6—Contd.

Capacity:—Nm <sup>3</sup> of gas produced per sq. meter of grate/hearth area/hr.	874	2000	2040
Nm <sup>3</sup> of CO & H <sub>2</sub> produced per square meter of grate (hearth) area/hr.	598	1890	1885
Carbon efficiency, %	58.0	95.0	95.0

\*Air is used during the operation of Semi-water gas plant.

TABLE 7—COST OF PRODUCTION OF SYNTHESIS GAS  
(Pilot Slagging Generator)

<b>Capital Cost:—</b>		
(a) Slagging Generator (b) Oxygen Pipe line (c) Equipments shed	} Rs. 4.5 Lakhs.	
<b>Basis: 40 M. Tonnes of Coke through-put per day.</b>		
<b>A. Raw materials.</b>		
		Rs.
(a) Coke—40 Tonnes/day. @ Rs. 65/- per tone	2,600	
(b) Blast furnace slag—11 tonnes/day. @ Rs. 12/- per tonne	132	
(c) Lime stone—7 tonnes/day. @ Rs. 25/- per tonne	175	
<b>B. Utilities</b>		
(a) Steam: 16.8 tonnes/day. @ Rs. 6=50/tonne	109	
(b) Oxygen—20,000 Nm <sup>3</sup> /day. @ Rs. 0.12/Nm <sup>3</sup>	2,400	
(c) Water—21,60,000 gallons/day. @ Rs. 0.40/ 1000 gallons	87	
(d) Power—522 KWH/day. @ Rs. 44/- per 1000 KWH	28	
<b>C. Operation and Maintenance</b>		
(a) Operational Labour: 50 Nos. @ Rs. 5/- per head	250	
(b) Maintenance @ 50% of operational labour cost:	125	
(c) Overhead charge @ 100% of direct labour cost	250	

**D. Fixed charge.**

(a) Maintenance: @ 3% Capital cost/year	37
(b) Services: @ 2% of capital cost/year	24

Total Works Cost	Rs. 6,217
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E. Depreciation: @ 10% Capital Cost/year	123
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Nett Cost	Rs. 6,340
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Production of CO & H<sub>2</sub> per day: 77,000 Nm<sup>3</sup>

Cost of Production of 1000 Nm <sup>3</sup> of CO & H <sub>2</sub>	Rs. 82.34
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# Catalytic Steam-Heptane Reaction

By

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A mechanism for the rate determining step in steam-heptane reaction at elevated temperatures and with high steam-heptane molar ratio has been postulated, and on that basis a theoretical relationship between the rate of reaction and the operating variables has been derived, which has been further tested experimentally under various operating conditions. The operating variables were, temperature, 590-785°C; total gas mean mass velocity, 180-600 lbs/(hr) (ft<sup>2</sup>); steam/heptane, 20-56 moles/mole; pressure, 1 atm; catalyst particles size, 0.0167-0.030 ft; catalyst packed volume,  $1.89 \times 10^{-3}$ – $4.5 \times 10^{-3}$  ft<sup>3</sup>; catalyst bed depth, 4.5-11.0 inches.

The theoretical expressions derived are for

$$(a) \frac{d_p G_m}{\mu} < 350.$$

$$r = C_1 \cdot \frac{G_m^{0.50} \cdot T^{0.21} \cdot (p_{CH_4} - p_{CH_4}^{eq.}) \text{ l.m.}}{d_p^{1.51} \cdot M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}}$$

$$\text{and for (b) } \frac{d_p G_m}{\mu} > 350$$

$$r = C_2 \cdot \frac{G_m^{0.50} \cdot T^{0.14} \cdot (p_{CH_4} - p_{CH_4}^{eq.}) \text{ l.m.}}{d_p^{1.41} \cdot M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}}$$

$$\text{Where, } C_2 = C_1 \cdot \frac{0.989}{1.820 \mu^{0.10}}$$

Under their experimental conditions, the results obtained by the authors indicated that  $\frac{d_p G_m}{\mu}$  values were always less than 350 and

$$r = 9.225 \times 10^{-3} \left( \frac{C_{H_2}}{C_{H_2O}} \right)^{0.662} \frac{G_m^{0.5} \cdot T^{0.21} \cdot (p_{CH_4} - p_{CH_4}^{eq.}) \text{ l.m.}}{d_p^{1.51} \cdot M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}}$$

$$\text{and } C_1 = 9.225 \times 10^{-3} \left( \frac{C_{H_2}}{C_{H_2O}} \right)^{0.662}$$

The rate expression for  $\frac{d_p G_m}{\mu} > 350$  has been represented by the following equation which on application to some commercial operational data was found satisfactory.

$$r = 5.0 \times 10^{-3} \left( \frac{C_{H_2}}{C_{H_2O}} \right)^{0.662} \frac{G_m^{0.50} \cdot T^{0.14} \cdot (p_{CH_4} - p_{CH_4}^{eq.}) \text{ l.m.}}{\mu^{0.10} d_p^{1.41} M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}}$$

## Introduction

Catalytic steam reforming of naphtha is being increasingly used for commercial production of synthesis gas for manufacture of ammonia, methanol etc. To study the effects of operating variables on the kinetics of catalytic steam reforming of naphtha at elevated temperatures it was decided to start with heptane steam reaction so as to eliminate the complexity involved in the composition itself of naphtha.

Heptane a saturated hydrocarbon of molecular weight 100 and C/H weight ratio 5.25, resembles naphtha in

the physico chemical properties relevant for the purpose of steam reforming reaction and as such a study of the kinetics of steam heptane reaction will be a direct measure of that of naphtha-steam reaction.

## Theory

In steam reforming of hydrocarbons at elevated temperatures, the composition of gas produced is ultimately controlled by methane-steam and carbon-monoxide steam reactions. Of these, the rate of methane-steam reaction is much slower, and for simplicity it

has been postulated that the rate determining reaction in steam-heptane reaction is the methane-steam reaction. The mechanism of the latter reaction has been postulated as that occurring by diffusion of methane molecules from gas bulk to the catalyst gas interface followed by chemical reaction with water molecules at this interface.

From the bench scale data it has been found that at the elevated temperature the rate of reaction is not sufficiently dependent on temperature and as such the overall reaction at elevated temperature seems to be controlled mainly by diffusion rather than by chemical reaction and therefore interfacial concentrations may be taken as equal to equilibrium concentration. The rate of reaction may then be represented by,

$$r = K_g a_v \pi (Y_{CH_4} - Y_{CH_4}^{eq}) = K_g a_v \pi (Y_{CH_4} - Y_{CH_4}^{eq}) \quad (1)$$

$$\text{NOW } a_v \propto \frac{1}{d_p} \quad (2)$$

and  $K_g$ , the mass transfer coefficient, for flow through packed bed is given by the following correlations.<sup>1</sup>

$$(i) \text{ for } \frac{d_p G_m}{\mu} < 350.$$

$$\left[ \frac{K_g P_m M_m}{G_m} \right] \left[ \frac{\mu}{\rho D} \right]^{2/3} = 1.820 \left[ \frac{d_p G_m}{\mu} \right]^{-0.51} \quad (3a)$$

$$(ii) \text{ for } \frac{d_p G_m}{\mu} > 350.$$

$$\left[ \frac{K_g P_m M_m}{G_m} \right] \left[ \frac{\mu}{\rho D} \right]^{2/3} = 0.989 \left[ \frac{d_p G_m}{\mu} \right]^{-0.41} \quad (3b)$$

Where for complex mixtures in which reaction of the type  $aA + bB = rR + sS$  takes place, mean partial pressure  $P_m$  has been given by Hougen and Watson<sup>2</sup> as  $\log$  mean of  $(\pi + p_a \delta A)$ ,  $\delta A = \frac{(r+s) - (a+b)}{a}$ . For methane steam reaction,  $CH_4 + H_2O = CO + 3H_2$ ,  $\delta A = 2$  and hence

$$P_m = (\pi + 2p_{CH_4}) l.m \quad (4)$$

From equations 1, 2, 3a, 3b, & 4 and since  $\mu$  is approximately proportional to  $T^{3/4}$ ,  $\rho \propto \frac{\pi}{T}$  and  $D \propto \frac{T^{3/2}}{\pi}$ , it is

possible to show that for  $\frac{d_p G_m}{\mu} < 350$ .

$$K_g a_v = C_1 \cdot \frac{G_m^{0.5} \cdot T^{0.21}}{d_p^{1.51} \cdot M_m \cdot (\pi + 2p_{CH_4}) l.m.} \quad (5a)$$

and for  $\frac{d_p G_m}{\mu} > 350$ .

$$K_g a_v = C_2 \cdot \frac{G_m^{0.59} \cdot T^{0.14}}{d_p^{1.41} \cdot M_m \cdot (\pi + 2p_{CH_4}) l.m.} \quad (5b)$$

$$\text{where } C_2 = \frac{0.989}{1.820 \mu^{0.10}} C_1 \quad (5c)$$

## Experimental

### Experimental set-up

The experimental set up comprises the following:

- (1) One insulated vaporiser, fitted with steam and heptane inlets, vapour outlet, vent, a thermometer pocket and packed with broken rasching rings to increase heat transfer rate. This is heated electrically.
- (2) One electrically heated stainless steel (type 321) preheater tube, 1 inch id, 2 ft long with a thermocouple well at its outlet end.
- (3) One electrically heated stainless steel (type NCT-3) reactor tube with a thermocouple well through the outlet end.
- (4) One water cooled copper coil condenser.
- (5) Two condensate receivers of glass.
- (6) One wet gasometer to meter the product gas.
- (7) One  $\frac{1}{8}$  inch orificemeter for steam.
- (8) One rotameter for measuring liquid heptane flow.

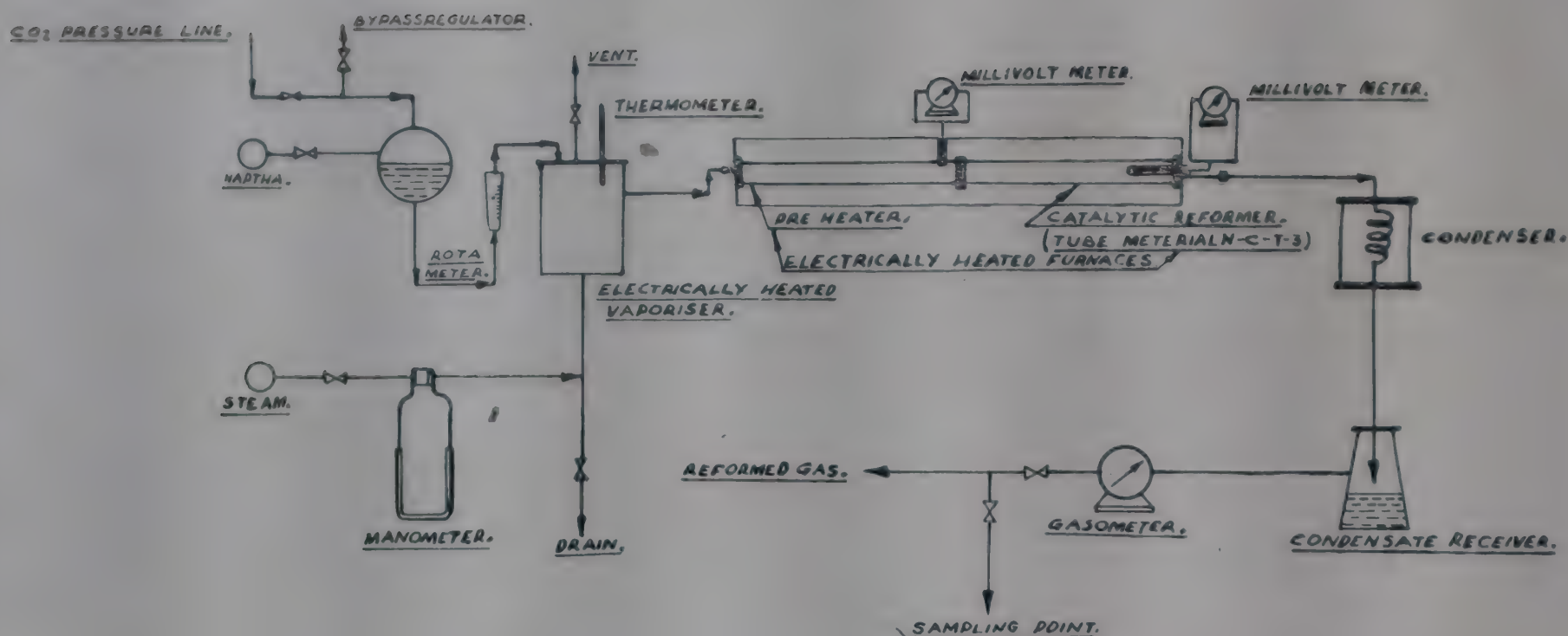
Before setting up the apparatus, the preheater and the reactor tubes were packed with  $\frac{1}{4}$  inch alundum balls and in between the alundum balls & the outlet end of the reactor was placed a layer of the reforming catalyst of known weight and size (Fig. 1). The preheater and reactor tubes were heavily insulated.

### Materials used

- (1) Heptane, commercially pure, sp gr 0.718, boiling range 93-94°C, olefins 5.5%, aromatics 6.5%.
- (2) Nickel Reforming catalyst (I.C.I. 22-1), hollow cylindrical rings (0.6 inch outer diameter, 0.3 inch internal diameter, 0.6 inch long), Ni content 15%. These were ground to smaller sizes for experimental use.
- (3) Reactor tube:- Stainless steel (type NCT-3), internal diameter 1 inch & 2 ft long.

### Procedure

After assembling the apparatus, the vaporiser, preheater and reactor were electrically heated initially to 110°, 350° & 450°C respectively, and then steam was



#### RANGE OF VARIABLES STUDIED.

1. TEMPERATURE	600°-800°C.
2. HYDROCARBON RATE	0.8-4g/min.
3. STEAM: CARBON, MOL/ATOM.	3-8
4. PRESSURE	ATMOSPHERIC

Fig. 1. Naphtha-Steam Reforming Unit.

introduced at the desired rate with simultaneous adjustment of condenser cooling water rate to get the condensate separated at room temperature. The preheater and the reactor were then gradually heated to 450°C and desired reaction temperature respectively. Heptane was then introduced, preheater temperature maintained at 450°C & reaction temperature maintained constant at desired value by varying current input to heater windings. The gas production rate was noted from the gas meter. Steady conditions indicated by constant gas make were obtained after 3-4 hours operation. This is due to the fact that the activation of catalyst surface by reduction with process gas containing hydrogen is enhanced only when the gas production rate becomes sufficiently high.

After the steady conditions were obtained, samples of gas and condensate were collected for definite time intervals and analysed. Two series of experiments using different amounts of catalyst were performed. During operation, precaution was always taken to ensure that the steam rate does not fall below twice that required for theoretical reaction (theoretical requirement is about 10.7 moles/mole heptane). The hydraulic binding agent

gives the catalyst a tendency to disintegrate if even momentarily insufficient steam is present<sup>3</sup>.

## Results

### Experimental data

Experimental data presented in Table 1 indicate the gas make and its composition for various heptane and steam rates at different temperatures. Experiments in series A were carried out with 45.66 gms catalyst of surface equivalent spherical diameter,  $d_p=0.0167$  ft, packed volume,  $1.89 \times 10^{-3}$  ft<sup>3</sup> and bed depth 4.5 inches while in series B with 112 gms catalyst of  $d_p=0.030$  ft, packed volume= $4.5 \times 10^{-3}$  ft<sup>3</sup> and bed depth=11.0 inches.

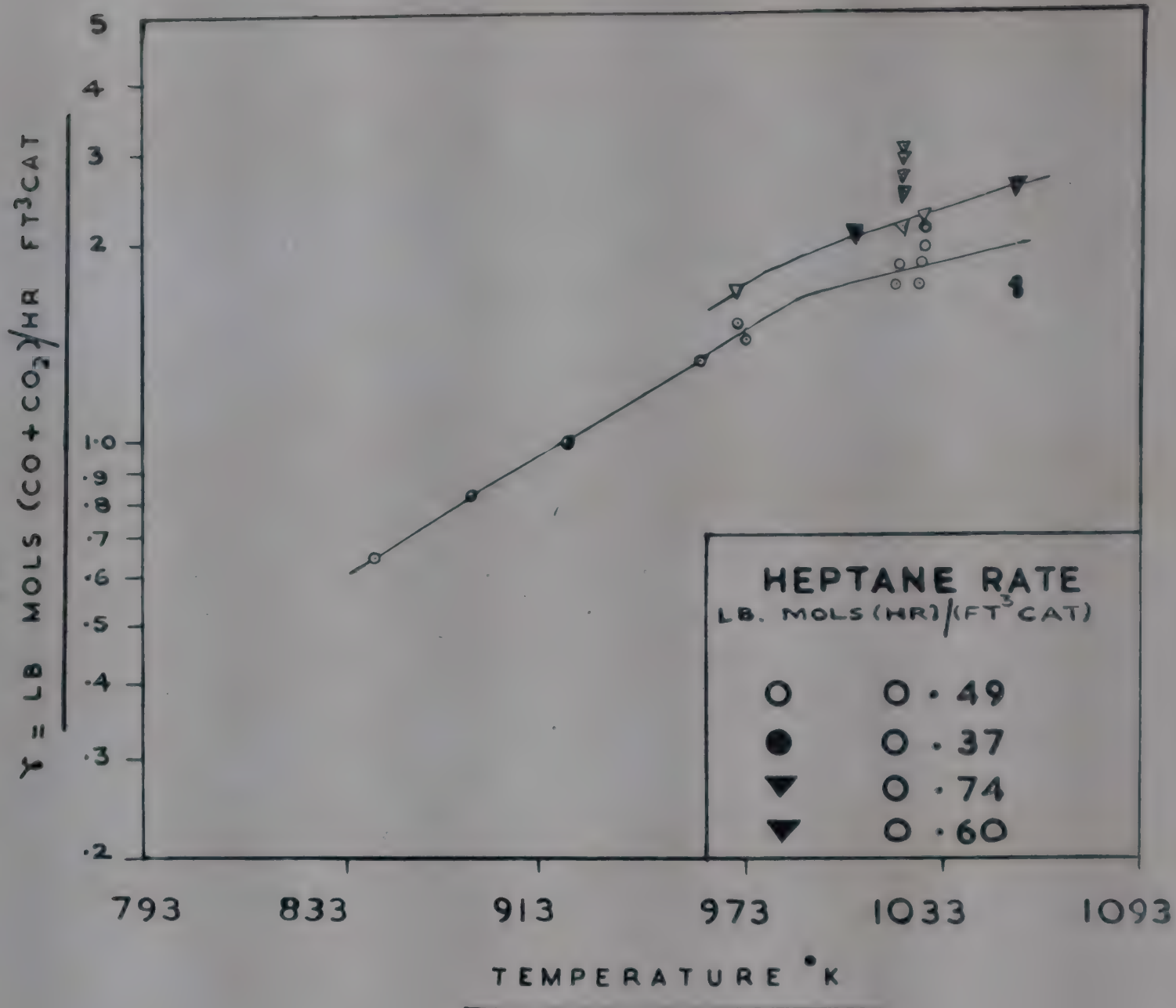
### Correlation of data

Table 2 shows the yields of CO+CO<sub>2</sub> as per cent equilibrium under operating conditions. For calculation of the equilibrium yields, the composition of commercially pure heptane was taken as C<sub>7</sub>H<sub>16</sub>, and the equilibrium composition of gas has been assumed as controlled by methane-steam reaction  $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$  & carbonmonoxide-steam reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . From the equilibrium constants of these two reactions

TABLE 1

Series	Expt. No.	Temp., °C	Heptane Feed Rate, g/min.	Steam Feed Rate, g/min.	Gas Produced c.f.m.	Condensate separated g/min.		Gas Composition, % (by vol.)				
						Aq. Layer	Hydro- carbon Layer	CO	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	Unsatds
A	1	700	2.58	17.70	0.2450	14.90	—	16.7	7.7	12.1	57.2	6.5
	2	695	1.55	13.80	0.1235	12.65	0.75	11.4	8.7	34.6	39.1	6.2
	3	695	3.24	20.80	0.2340	18.35	0.15	13.1	5.8	17.9	58.8	4.4
	4	760	2.88	17.60	0.3220	13.85	—	10.1	8.9	15.2	60.5	5.4
	5	765	1.44	13.60	0.2650	12.40	—	11.4	10.6	9.7	63.4	4.8
	6	765	1.08	9.40	0.1775	6.60	—	11.9	12.3	4.4	67.7	4.3
	7	765	3.24	20.80	0.3680	17.90	—	11.9	11.7	7.8	61.5	7.1
	8	700	1.12	9.50	0.1410	7.60	—	8.8	13.1	9.8	64.7	3.3
	9	720	1.62	13.60	0.1790	12.10	—	8.3	15.5	36.8	35.2	4.2
B	1	760	2.51	17.60	0.3000	14.00	—	13.6	10.9	22.7	50.2	2.6
	2	760	1.65	12.20	0.2060	9.64	—	11.2	14.1	8.9	64.4	1.5
	3	760	2.05	14.00	0.3530	9.68	—	14.1	13.6	10.3	60.6	1.5
	4	760	2.51	18.00	0.4000	13.90	—	12.2	15.5	14.8	55.6	2.0
	5	760	3.06	22.00	0.4170	18.00	—	11.4	16.7	21.2	50.6	0.1
	6	730	1.24	7.50	0.1900	5.28	—	11.32	16.35	16.35	55.4	0.42
	7	735	2.05	15.00	0.2520	11.35	—	12.75	14.82	24.55	45.8	2.08
	8	735	0.73	6.60	0.1380	5.35	—	7.60	19.65	13.96	58.7	0.22
	9	715	0.90	8.00	0.1565	9.75	—	8.00	18.8	17.30	55.1	0.90
	10	705	1.65	12.10	0.1750	10.25	—	8.9	17.8	31.2	39.0	1.8
	11	705	2.50	18.30	0.1750	16.50	—	9.2	17.7	28.5	41.7	3.3
	12	785	1.24	8.20	0.2070	6.85	—	12.4	14.8	10.1	61.8	0.9
	13	785	2.05	15.40	0.3140	12.16	—	11.2	14.9	8.8	64.2	1.0
	14	785	0.60	6.60	0.0940	6.33	—	7.6	17.8	6.2	68.0	0.4
	15	760	1.65	16.80	0.2000	15.20	—	10.0	12.7	14.4	60.1	2.7
	16	760	1.65	10.40	0.2320	7.75	—	10.6	14.8	19.5	52.7	2.5
	17	760	1.65	13.50	0.2230	11.80	—	10.3	15.8	14.6	57.5	1.9
	18	760	1.65	11.80	0.2500	9.20	—	10.7	16.1	14.1	56.3	2.5
	19	755	1.65	11.00	0.2300	8.67	—	12.3	14.4	5.3	66.0	2.3
	20	755	2.51	12.80	0.2600	10.40	—	13.7	13.9	19.4	50.0	3.1
	21	750	2.51	10.40	0.3370	7.90	—	17.5	10.8	21.8	48.7	1.7
	22	750	2.51	11.20	0.3150	8.53	—	12.9	14.3	21.1	49.2	2.5
	23	750	2.51	13.00	0.3000	10.58	—	11.4	15.7	27.9	42.6	2.5
	24	705	1.65	11.70	0.2000	9.53	—	9.0	17.9	6.1	65.0	2.0
	25	700	2.51	18.40	0.2140	16.10	—	8.1	17.8	34.8	36.5	2.6
	26	785	1.24	9.00	0.2000	7.00	—	12.5	15.7	14.5	55.7	1.7
	27	705	0.89	8.00	0.1000	6.60	—	7.3	19.2	20.4	50.8	2.3
	28	755	1.65	11.80	0.2140	9.30	—	11.8	16.4	20.1	49.6	2.1
	29	705	1.65	13.60	0.1760	12.00	—	9.1	18.3	29.0	41.2	2.4
	30	690	1.65	13.60	0.1620	12.00	—	7.3	18.1	20.3	52.2	2.1
	31	680	1.65	13.60	0.1460	12.25	—	6.9	18.6	18.6	52.7	3.1
	32	650	1.65	13.60	0.1380	12.25	—	6.3	20.2	22.2	48.8	2.6
	33	620	1.65	13.60	0.1080	12.85	—	5.2	20.6	33.4	37.3	3.4
	34	590	1.65	13.60	0.0945	13.17	—	4.1	17.9	33.6	41.1	3.5

Fig. 2. Effect of Temperature on Rate of Reaction



$Y = \text{LB MOLS}(\text{CO} + \text{CO}_2) / \text{HR FT}^3 \text{ CAT.}$

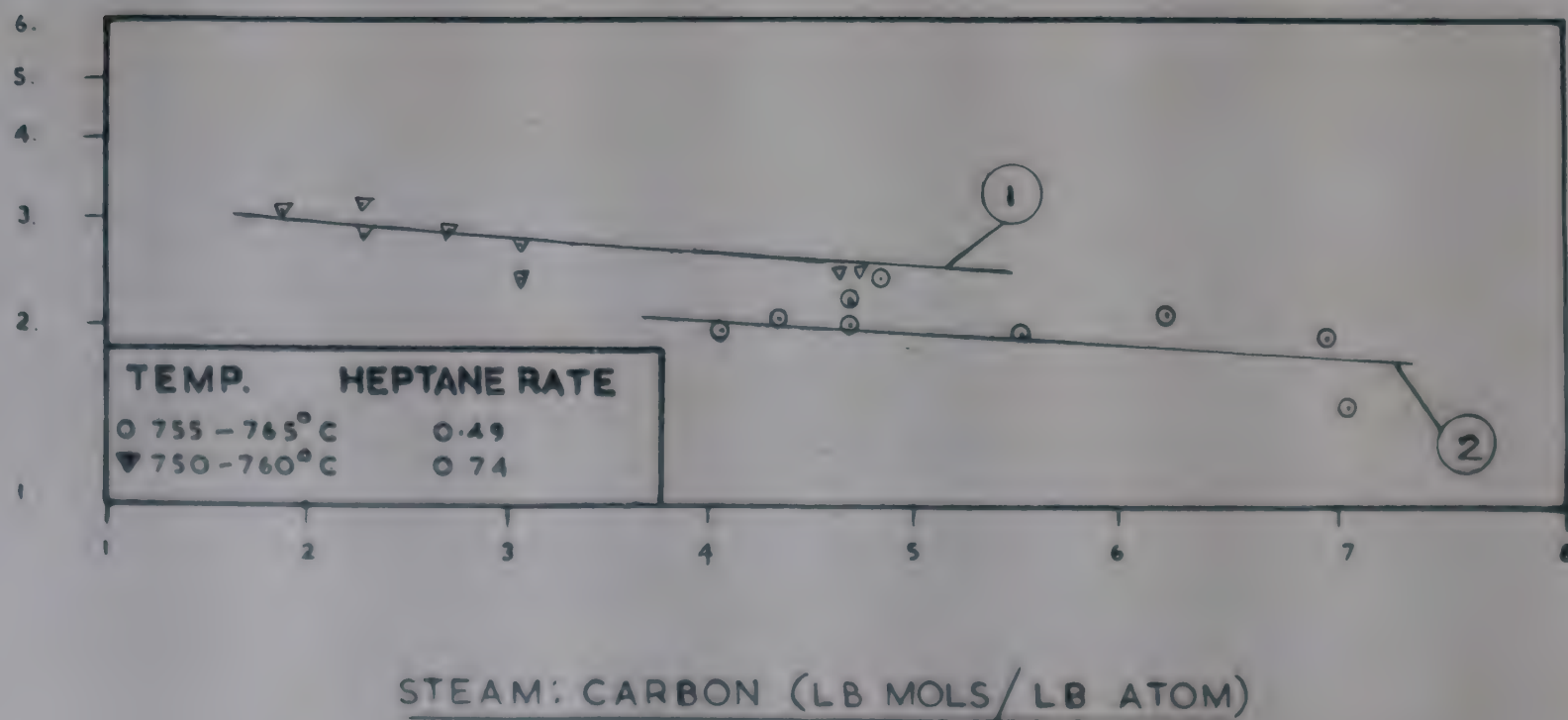


Fig. 3. Effect of Steam-Carbon Ratio on Rate of Reaction.

and from material balances the equilibrium yields of gas components can be calculated. These equilibrium yields show a general decrease with increase in heptane feed rate but cannot be correlated simply with heptane rate. Fig. 2 shows the effect of temperature on reaction rate expressed as moles (CO+CO<sub>2</sub>) per hour per ft<sup>3</sup> catalyst.

The reaction rate expressed in this way is a true measure of reaction of hydrocarbon with steam. Effect of temperature on rate of reaction is not sufficiently high and the reaction rate in the present experimental temperature range seems to be controlled more by diffusion than by chemical kinetics.

The same reaction rate has been plotted against steam/

TABLE 2

Series	Expt. No.	Steam/Carbon lb moles/atom	Heptane Feed Rate, lb moles/hr (ft <sup>3</sup> Cat)	lb moles (CO + CO <sub>2</sub> )/hr. (ft <sup>3</sup> Cat)		Yield of (CO + CO <sub>2</sub> ) % equilibrium
				Experimental	Equilibrium	
A	1	5.45	1.80	4.82	12.6	38.2
	2	7.10	1.08	1.91	7.6	25.1
	3	5.13	2.27	3.44	15.9	21.6
	4	4.83	2.02	4.70	14.2	33.1
	5	7.56	1.00	4.50	7.0	64.3
	6	6.93	0.76	3.32	5.33	62.3
	7	5.00	2.27	6.65	15.9	41.7
	8	6.75	0.79	2.39	5.55	43.1
	9	6.67	1.14	3.21	8.0	40.0
B	1	5.54	0.74	2.38	5.19	45.7
	2	5.81	0.49	2.34	3.44	68.0
	3	5.38	0.60	2.35	4.20	55.8
	4	5.65	0.74	2.42	5.19	46.5
	5	5.67	0.90	2.35	6.30	37.2
	6	4.76	0.365	1.70	2.56	66.4
	7	5.75	0.59	2.26	4.13	54.7
	8	7.15	0.215	1.215	1.51	80.5
	9	7.00	0.263	1.355	1.84	73.7
	10	5.80	0.485	1.515	3.39	44.7
	11	5.67	0.737	1.525	5.15	29.6
	12	5.22	0.366	1.82	2.56	71.2
	13	5.91	0.605	2.64	4.25	62.0
	14	8.70	0.180	0.76	1.26	60.5
	15	8.05	0.487	1.47	3.40	43.2
	16	4.97	0.487	1.91	3.40	56.2
	17	6.45	0.487	1.88	3.40	55.3
	18	5.65	0.487	2.17	3.40	64.0
	19	5.27	0.487	1.99	3.40	58.5
	20	4.02	0.74	2.33	5.17	45.6
	21	3.27	0.74	3.08	5.17	60.5
	22	3.52	0.74	2.78	5.17	54.5
	23	4.08	0.74	2.64	5.70	51.7
	24	5.60	0.49	1.74	3.43	50.6
	25	5.77	0.74	1.80	5.18	34.6
	26	5.72	0.37	1.83	2.59	70.7
	27	7.10	0.26	0.85	1.62	52.3
	28	5.62	0.49	1.95	4.43	56.8
	29	6.47	0.487	1.60	3.40	47.0
	30	6.47	0.487	1.33	3.40	39.0
	31	6.47	0.487	1.03	3.40	30.3
	32	6.47	0.487	1.02	3.40	30.0
	33	6.47	0.487	0.83	3.40	24.4
	34	6.47	0.487	0.65	3.30	19.4

carbon ratio, moles/atom, which indicates that increase in steam/carbon ratio tends to decrease slightly the steam-heptane reaction rate (Figure 3). This might possibly be due to decrease in the active fraction of the catalyst surface,  $a_v$  with increase in steam concentration. It has been shown later that the rate of reaction is dependent on  $C_{H_2}/C_{H_2O}$  ratio.

#### Application of Theory for correlation of experimental results

Since  $Y_{CH_4}^{eq}$  is constant at a particular temperature and pressure we can take log mean average value for driving force between inlet and outlet of the bed and hence equation (1) becomes

$$\begin{aligned} r &= K_g a_v \pi (Y_{CH_4} - Y_{CH_4}^{eq}) \text{ l.m.} \\ &= K_g a_v \pi (p_{CH_4} - p_{CH_4}^{eq}) \text{ l.m.} \end{aligned} \quad (6)$$

For the present series of experiments the values of  $\frac{d_p G_m}{\mu}$  were lower than 350 and hence substituting for  $K_g a_v$  by equation (5a) we get

$$r = C_1 \cdot \frac{G_m^{0.5} \cdot T^{0.21} \cdot (p_{CH_4} - p_{CH_4}^{eq}) \text{ l.m.}}{d_p^{1.51} \cdot M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}} \quad (7)$$

Where  $r$ , the rate of reaction is expressed as lb moles  $(CO + CO_2)$  per hour per  $ft^3$  catalyst. Equation (7) offers a simple basis for correlation of experimental results. In the present series of experiments  $p_{CH_4}$  is almost equal to zero and hence

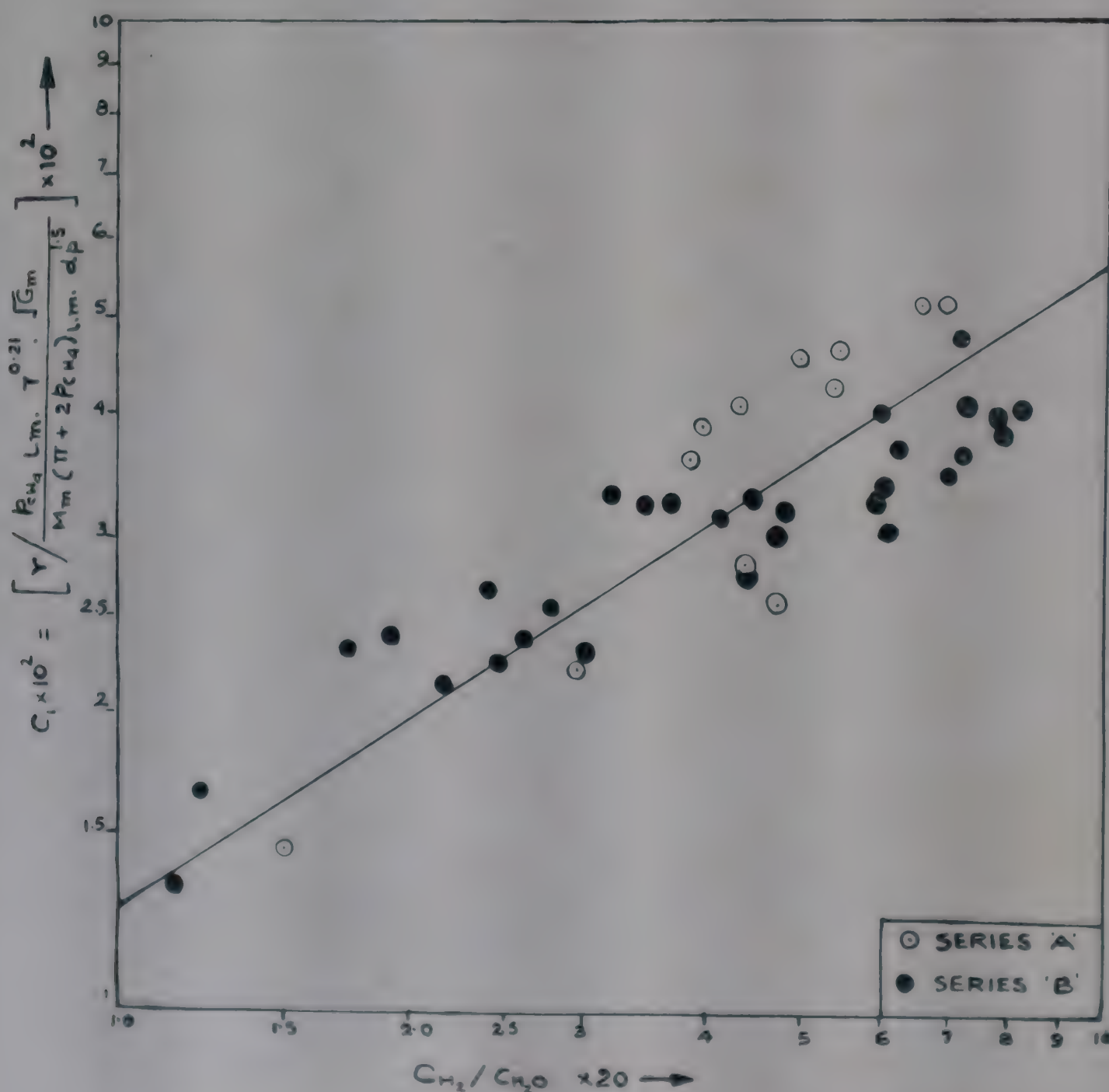


Fig. 4. Generalised Correlation of Experimental Data: Dependence of Rate on the Ratio of  $C_{H_2}/C_{H_2O}$ .

$$C_1 = \frac{r}{G_m^{0.5} \cdot T^{0.21} \cdot p_{CH_4} \cdot l.m.} \quad (8)$$

$$d_p^{1.51} \cdot M_m \cdot (\pi + 2p_{CH_4}) \cdot l.m.$$

It was found that the value of  $C_1$  is not constant but depends on the ratio  $\frac{C_{H_2}}{C_{H_2O}}$  (Table 3). A straight line correlation has been obtained with  $C_1$  against  $C_{H_2}/C_{H_2O}$  in a logarithmic graph (Fig. 4) which may be

expressed as,

$$C_1 = 9.225 \times 10^{-2} \left( \frac{C_{H_2}}{C_{H_2O}} \right)^{0.662} \quad (9)$$

$$\text{Hence, } r = 9.225 \times 10^{-2} \left( \frac{C_{H_2}}{C_{H_2O}} \right)^{0.662} \times$$

$$\frac{G_m^{0.5} \cdot T^{0.21} \cdot p_{CH_4} \cdot l.m.}{d_p^{1.51} \cdot M_m \cdot (\pi + 2p_{CH_4}) \cdot l.m.} \quad (10)$$

TABLE 3

Series	Expt. No.	$G_m$ , lbs/ hr (ft <sup>3</sup> )	'r' lb. moles CO + CO <sub>2</sub> /hr (ft <sup>3</sup> Cat)	$p_{CH_4}$ l.m. $M_m(\pi + 2p_{CH_4}) \cdot l.m.$	$T^{0.21}$	$1/d_p^{1.51}$	$C_{H_2}/C_{H_2O}$	$C_1 \times 10^2$
A	1	474	4.82	$3.05 \times 10^{-3}$	4.25	$2.5 \times 10^3$	0.191	3.62
	2	384	1.91	$3.29 \times 10^{-3}$	4.25	"	0.075	1.45
	3	560	3.44	$3.22 \times 10^{-3}$	4.25	"	0.148	2.23
	4	452	4.70	$3.83 \times 10^{-3}$	4.30	"	0.217	2.85
	5	368	4.50	$2.60 \times 10^{-3}$	4.30	"	0.266	4.37
	6	227	3.32	$2.18 \times 10^{-3}$	4.30	"	0.356	4.90
	7	557	6.65	$2.85 \times 10^{-3}$	4.30	"	0.246	4.62
	8	236	2.39	$2.98 \times 10^{-3}$	4.25	"	0.235	2.60
	9	374	3.21	$4.02 \times 10^{-3}$	4.27	"	0.105	2.04
B	1	486	2.38	$4.12 \times 10^{-3}$	4.30	$1.92 \times 10^3$	0.204	3.17
	2	345	2.34	$3.04 \times 10^{-3}$	4.30	"	0.360	3.66
	3	387	2.35	$3.50 \times 10^{-3}$	4.30	"	0.410	4.12
	4	507	2.42	$3.80 \times 10^{-3}$	4.30	"	3.300	3.40
	5	626	2.35	$4.09 \times 10^{-3}$	4.30	"	0.220	2.78
	6	208	1.70	$4.48 \times 10^{-3}$	4.28	"	0.394	4.04
	7	400	2.26	$4.18 \times 10^{-3}$	4.28	"	0.184	3.30
	8	181	1.215	$3.34 \times 10^{-3}$	4.28	"	0.295	3.30
	9	258	1.355	$3.12 \times 10^{-3}$	4.26	"	0.173	3.32
	10	335	1.515	$4.19 \times 10^{-3}$	4.25	"	0.131	2.41
	11	492	1.525	$3.56 \times 10^{-3}$	4.25	"	0.087	2.35
	12	235	1.820	$3.41 \times 10^{-3}$	4.32	"	0.363	4.18
	13	414	2.640	$2.95 \times 10^{-3}$	4.32	"	0.322	5.30
	14	181	0.760	$1.73 \times 10^{-3}$	4.32	"	0.197	3.94
	15	448	1.47	$2.60 \times 10^{-3}$	4.30	"	0.160	3.38
	16	286	1.91	$4.46 \times 10^{-3}$	4.30	"	0.306	3.09
	17	370	1.88	$2.84 \times 10^{-3}$	4.30	"	0.213	4.17
	18	324	2.17	$3.58 \times 10^{-3}$	4.30	"	0.298	4.10
	19	300	1.99	$2.60 \times 10^{-3}$	4.30	"	0.342	5.30
	20	365	2.33	$4.58 \times 10^{-3}$	4.30	"	0.240	3.24
	21	321	3.08	$5.43 \times 10^{-3}$	4.30	"	0.399	3.84
	22	335	2.78	$5.24 \times 10^{-3}$	4.30	"	0.352	3.53
	23	383	2.64	$5.34 \times 10^{-3}$	4.30	"	0.235	3.06
	24	314	1.74	$2.52 \times 10^{-3}$	4.25	"	0.270	4.77
	25	499	1.80	$4.07 \times 10^{-3}$	4.25	"	0.096	2.42
	26	248	1.83	$3.74 \times 10^{-3}$	4.32	"	0.310	3.74
	27	209	0.85	$3.10 \times 10^{-3}$	4.25	"	0.150	2.32
	28	320	1.95	$4.00 \times 10^{-3}$	4.30	"	0.220	3.31
	29	371	1.60	$3.78 \times 10^{-3}$	4.25	"	0.121	2.69
	30	363	1.33	$3.27 \times 10^{-3}$	4.24	"	0.139	2.56
	31	363	1.03	$2.96 \times 10^{-3}$	4.23	"	0.124	2.26
	32	363	1.02	$3.07 \times 10^{-3}$	4.20	"	0.108	2.17
	33	364	0.83	$3.28 \times 10^{-3}$	4.17	"	0.0615	1.67
	34	366	0.65	$3.085 \times 10^{-3}$	4.14	"	0.0582	1.325

In the evaluation of  $p_{CH_4}$ , l.m. methane concentration at the inlet to the catalyst bed has been assumed in all cases based on the following arbitrarily chosen reaction, namely



where  $x$  = moles of steam per mole heptane. So that methane concentration at the inlet to the bed is  $5/(5+x)$  moles per total mole. This assumption of inlet methane concentration has served satisfactorily the purpose of correlating the present series of experimental data. It may be mentioned here that the theoretical rate of reaction calculated on this assumption agrees closely with some actual commercial plant data.

#### Application of derived relation to commercially operating plant data

Under commercially operating conditions the values of  $\frac{d_p G_m}{\mu}$  are always higher than 350. Hence substituting equations 5b, & 5c in equation (1) the following expression is obtained.

$$r = \frac{0.989}{1.820 \mu^{0.10}} \cdot C_1 \cdot \frac{G_m^{0.59} \cdot T^{0.14} \cdot (p_{CH_4} - p_{CH_4}^{eq}) \text{ l.m.}}{d_p^{1.41} \cdot M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}} \quad (12)$$

Substituting the value of  $C_1$  from equation (9), the predicted rate equation becomes

$$r = 5.0 \times 10^{-3} \left( \frac{C_{P_2}}{C_{H_2O}} \right)^{0.062} \times \frac{G_m^{0.59} \cdot T^{0.14} \cdot (p_{CH_4} - p_{CH_4}^{eq}) \text{ l.m.}}{\mu^{0.10} d_p^{1.41} \cdot M_m \cdot (\pi + 2p_{CH_4}) \text{ l.m.}} \quad (13)$$

The actual value for a commercial plant<sup>4</sup> using I.C.I. catalyst 22-5, differs by 8.3% from the value predicted by equation (13) which is based on experimental data using I.C.I. catalyst 22-1 indicating a fair agreement (Table 4). For a commercial plant<sup>5</sup> using Girdler catalyst, a deviation of 31% in the value of  $r$  was observed. This might be due to difference in activities of the catalysts.

TABLE 4—COMMERCIAL PLANT DATA IN STEAM REFORMING OF NAPHTHA

	Plant using ICI Catalyst	Plant using Girdler Catalyst
Naphtha feed/unit—	10,541 Kg/hr	2225 Kg/hr
Reformer tubes unit		
Nos	208	176
Size	4" i.d.	3½" i.d.
Fired length	21.3 ft	9' 10"

Outlet temperature	810°C	870°C
Mean Pressure in the catalyst bed	22 Kg/cm <sup>2</sup>	12.35 Kg/cm <sup>2</sup>
Equilibrium partial pressure of Methane at outlet conditions	0.85 atm	0.017 atm
Catalyst	Nickel catalyst	Nickel catalyst
Surface equivalent spherical diameter of catalyst	0.07 ft	0.0283 ft
Mass velocity of Gas Steam mixture	6500 lbs/hr ft <sup>2</sup>	2900 lbs/hr ft <sup>2</sup>
Mean molecular weight of gas-steam mixture	15	15
lb moles steam per lb atom C	3.16	5.0
Outlet gas composition, per cent—		
CO <sub>2</sub>	14.82	27.7
CO	13.36	
H <sub>2</sub>	63.50	71.5
N <sub>2</sub>	0.40	—
CH <sub>4</sub>	7.90	0.8
Steam/gas	0.69	1.0
Viscosity of outlet gas-steam mixture	0.0945 lb/(ft)(hr)	0.102 lb/(ft)(hr)
$\frac{d_p G_m}{\mu}$	4820	807
lb moles (CO + CO <sub>2</sub> )		
(hr) (ft <sup>3</sup> cat)		
Plant data	3.4	2.9
lb moles CO + CO <sub>2</sub>		
(hr) (ft <sup>3</sup> cat)		
predicted by eqn. (13) <sup>f</sup>	3.14	4.2
Per cent deviation of Plant data from predicted data	8.3%	31%
Naphtha Specifications C/H	5.25	5.25
Mol wt	100	100

#### Conclusions

From the experimental data the generalised correlations, viz. equations 10 & 13 have been developed which not only satisfy the various conditions of the present experiments but are also applicable for commercial operating conditions. In the derivation of the above

equations, the following postulates have been made, (a) the rate is determined mainly by diffusion and not by chemical reaction kinetics, and (b) methane concentration at the inlet to the catalyst bed has been assumed according to equation (11) for calculating log mean methane concentration between the inlet & outlet of the bed.

Based on the above postulates it has been found that the ratio  $\frac{C_{H_2}}{C_{H_2O}}$  has a significant bearing on the rate of reaction. This ratio may perhaps determine the stages of oxidation and reduction of catalyst surface and hence its surface activity as the rate has been found to be directly proportional to  $\left(\frac{C_{H_2}}{C_{H_2O}}\right)^{0.662}$ .

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### Nomenclature:

- $a_v$  = external surface of catalyst,  $ft^2/ft^3$   
 $C_{H_2}$  = concentration of Hydrogen in outlet gas,  
 lb moles.  
 $ft^3$   
 $C_{H_2O}$  = concentration of water vapour in outlet gas,  
 lb moles  
 $ft^3$

$D$  = diffusivity,  $ft^2/hr$ .

$d_p$  = surface equivalent spherical diameter of catalyst,  $ft$ .

$G_m$  = total mean gas mass velocity,  $lbs/(hr) (ft^2)$ .

$K_g$  = mass transfer coefficient,  $lb\ moles/(hr) (ft^2) \cdot atm$

$M_m$  = mean molecular weight.

$P_{CH_4}$  = partial pressure of methane,  $atm$ .

$r$  = rate of reaction,  $lb\ moles/(hr) (ft^3)\ catalyst$

$T$  = temperature,  $^{\circ}K$ .

$Y_{CH_4}$  = molefraction methane,  $lb\ mole/lb\ mole$ .

$\pi$  = total pressure,  $atm$ .

$\mu$  = viscosity,  $lb/(ft) (hr)$

$\rho$  = density of gas mixture,  $lbs/ft^3$

### Subscripts & Superscripts

$l.m.$  = log mean

$eq$  = equilibrium

$i$  = interface.

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# Studies on Corrosion of Mild Steel under Certain Plant Conditions - I: Ammoniacal Liquor

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Cracking of mild steel due to corrosion by regenerated ammoniacal liquor used in the CO<sub>2</sub> Scrubbing Section in one of the ammonia plants has been investigated by x-ray diffraction method which revealed the presence of different crystalline phases in the corroded products. Corrosion has been found to be due to the dissolved compounds like hydrogen sulphide, hydrocyanic acid and carbon dioxide, etc.

## Introduction

Corrosion of material of construction has been a problem since the inception of the chemical industries. But mild steel has been known to have only very little effect of corrosion by ammonia, and so it has been widely used in the ammonia industry. On the other hand, if one or more of the chemical agents like carbon dioxide, oxygen, hydrogen sulphide, etc. are present in the ammonia liquor, the ferrite and pearlite grains of mild steel may be affected to some extent.

It was expected that analysis and identification of the corrosion products, and a knowledge about their nature and state of aggregation by the physical methods can throw some light on the causes of corrosion. Hence spectroscopic, microscopic and x-ray diffraction studies were made on the various specimens to know the cause of corrosion of mild steel by ammoniacal liquor used in the CO<sub>2</sub> scrubbing section in one of the F.C.I.'s ammonia plants.

The arrangement for the removal of carbon dioxide

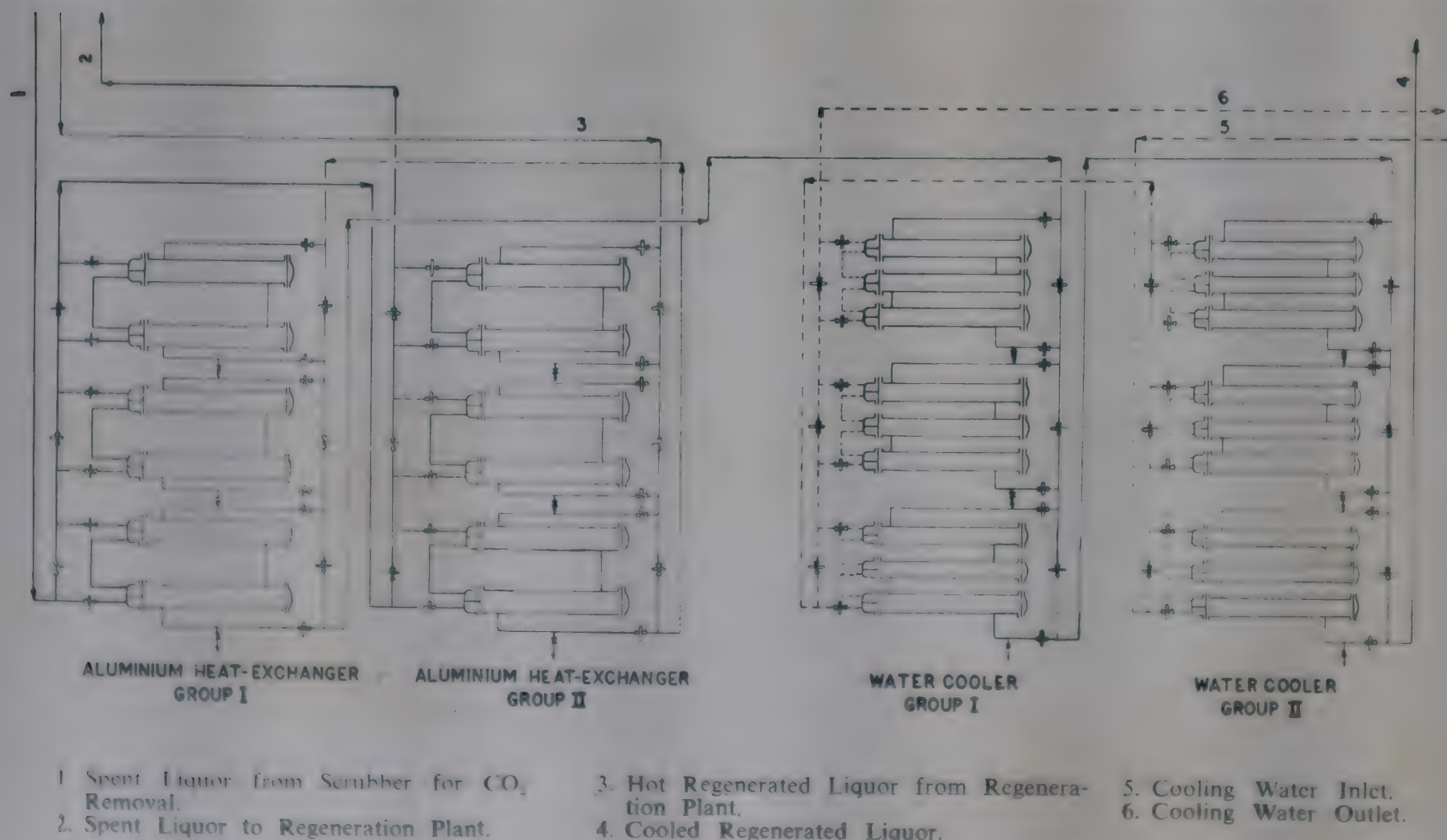


Fig. 1. Regenerated Liquor Cooling Section of CO<sub>2</sub> Removal Plant.

from coke oven gas is by scrubbing it with ammoniacal liquor. The spent ammoniacal liquor is regenerated by heating it indirectly with steam to a temperature of 87° to 89°C for carbon dioxide removal and then cooling in two stages viz. (1) by exchanging heat with spent liquor to be regenerated in a series of aluminium heat exchangers and then (2) by cooling with process water in a series of heat-exchanger type cooler made of mild steel (Fig. 1). The ammonia gas obtained from the spent liquor during regeneration is again dissolved in the cooled regenerated liquor to be used again for carbon dioxide scrubbing.

In the coolers, the water flows through the tube sides and the regenerated liquor through the shell sides. The terminal operating pressures for the shell sides are 1 Kg/cm<sup>2</sup> and atm. and for the tube sides 3.8 Kgs/Cm<sup>2</sup> and atmospheric. The quantity of regenerated liquor cooled is about 100 m<sup>3</sup>/hr.

In these coolers, corrosion cracking has been observed on the portions wherever the regenerated liquor is in contact with the metal, especially on the welded portions of the shells and headers and also on the tube sides. Moreover, cracking is observed mainly on the warmer portions of the set of coolers where the temperature of the cooled liquor is 60-65°C at the inlet and 30-35°C at the outlet.

*Description of the Samples:* The details of the samples, taken from various portions of the coolers, are given below (Table 1; Figs. 2A, 2B & 2C).

### Experimental Procedure & Results

The Drillings from the bulk material as well as scrapings from the corroded surface were obtained from all the samples. Prior to x-ray studies, a spectroscopic analysis of all the test pieces and scrapings were obtained (Table 2).

A visual inspection of the corroded surface of all the samples under a microscope by reflected light gave a preliminary idea about the presence of various compounds by their characteristic colours as given below:

1. Iron Oxides—by light and dark brown colours.
2. Iron Sulphides—by bright yellow colour.
3. Cyanides of Iron—by green and bluish green colours.

X-ray diffraction photographs of the drillings and scrapings in sealed Lindemann capillaries, were taken in a powder camera of 57.3 mm dia. with Zr-filtered Mo K $\alpha$  radiation at 45 KV and 18 mA tube current. The films were processed under standard conditions



FIG. 2A.

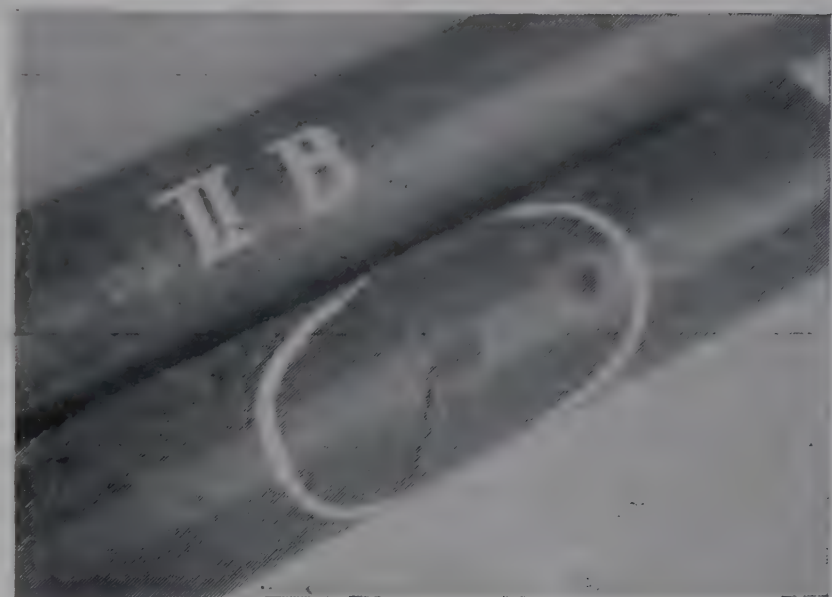


FIG. 2B.



FIG. 2C.

Figs. 2A, 2B and 2C. Samples of Mild Steel from Various Portions of Coolers (see Table 1).

TABLE 1—DETAILS OF SAMPLES OF CUT-PIECES

Sample No.	Material & Specn. No.	Location in the Coolers	Remarks
IA	Mild steel 37.21 DIN.	From T-Tube of the header towards inlet of the warmest cooler	Thickness-1/4" cracked on either sides of welding and badly rusted (Fig. 2A).
IB	Mild steel 37.21 DIN.	For a T-tube of header of another warmest cooler; from the same place as IA	Thickness-1/4"; no visible cracks; broken into two, along welding when attempted to cut the piece; badly rusted.
IIA	Mild steel 35.29 DIN.	From a cooler tube through which process water was sent	Thickness-1/6" pitted and cracked over the outer surface (Fig. 2B)
IIB	Mild steel 35.29 DIN	From the same cooler tube as IIA, but from a different region	Thickness-1/16"; pitted but no visible cracks Fig. (2B).
IIIA	Mild steel 35.29 DIN.	From a different cooler tube of the type from where IIA was obtained	Thickness-1/16", pitted and cracked over the surface of the tube (Fig. 2C).
IIIB	Mild steel 35.29 DIN.	From the same cooler as IIIA, but from a different region	Thickness-1/16"; pitted but no visible cracks.
IV	Mild steel 35.29 DIN.	From shell side of the warmest cooler	Thickness-1/4"; pitted severely and the surface covered with brown, dark brown, and grey, greenish and bluish coloured materials.

TABLE 2—SPECTROSCOPIC ANALYSES DATA OF CORROSION SAMPLES

No.	Samples	Minor elements 1.0 to 0.01% approxly	Trace elements Below .01% approxly	Remarks
1.	IB. inner core.	Mn, Si, Cu.	Cr, Ni, Mo, Co, Al, B.	Cu may be in traces also.
2.	IIB inner core.	Mn, Si, Cu.	Cr, Ni, Mo, Co, Al, B.	Cu may be in traces also.
3.	IIIB inner core.	Mn.	Si, Cu, Cr, Ni, Mo, Co, Al, B.	Cu & Si very low compared to IB & IIB.
4.	Welding material from header. (Inner core).	Mn, Si.	Cu, Ni, Mo, Co, Al, B.	—
5.	Scrapings from weld.	Mn, Si, Al, Cu, Ti.	Mg, Ca, Na, V, Ni, Cr, Mo, Zn, B.	
6.	Scrapings away from weld.	Mn, Si, Al, Cu, Ti.	Mg, Ca, Na, V, Ni, Cr, Sn, B.	Cu may be in traces.
7.	Scrapings from header (Un-cracked).	Mn, Si, Al, Cu, Ti.	Ca, Mg, Na, Ni, Cr, B.	Ti & Cu may be in traces.
8.	Scrapings from IIIA.	Mn, Si, Al, Cu.	Ti, Ca, Mg, Na, Ni, Cr, B.	Cu may be in traces.

Phosphorous, sulphur and carbon cannot be detected by the present facilities available.

TABLE 3—CRYSTALLINE PHASES DETECTED IN THE SCRAPINGS OF DIFFERENT SAMPLES

Sample No.	Major Phase	Minor Phase	Trace
IA	* Magnetite	Iron ferro-cyanide	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
IB	"	Iron ferro-cyanide	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
IIA	"	—	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
IIB	"	—	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
IIIA	"	—	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
IIIB	"	—	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
IV	"	Iron ferro-cyanide	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>

and the intensity of various diffraction lines were estimated visually.

The bulk material of all the samples constitutes mainly  $\alpha$ -Fe, while scrapings revealed various crystalline phases (Table 3). The x-ray data are presented in Table 4.

It is evident from Table 3 that scrapings from each sample contain large amounts of Fe<sub>3</sub>O<sub>4</sub> and small amounts of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Further, the samples IA, IB and IV are found to contain a minor crystalline phase,

TABLE 4—X-RAY DATA OF CORROSION SAMPLES

Bulk material from sample no. IA <sup>a</sup>	$\alpha$ -Fe ASTM, 6-0696	Scrapings from cracked and wel- ded portions of IA	Scrapings from non-welded por- tions of IB	Scrapings from sample no. IIAb	Scrapings from sample no. IV	$Fe_3O_4$ ASTM, 7-322	$\alpha$ - $Fe_2O_3$ <sup>c</sup>	$Fe_3[Fe(CN)_6]_3$ ASTM, 1-0239	Dark material from corrosion experiment.d
$d(\text{\AA})$	Int.	$d(\text{\AA})$	Int.	$d(\text{\AA})$	Int.	$d(\text{\AA})$	Int.	$d(\text{\AA})$	Int.
2.06	s	2.0268	100	2.158	vvw				
				3.55	vw	3.54	vvw	3.55	vvw
				2.55	vvw	2.56	vvw	2.55	vvw
				2.52	s, br	2.52	s, br	2.52	s, br
				2.197	w	2.197	w	2.269	vvw
				2.173	vvw	2.173	vvw	2.097	50
				1.968	vvw	1.968	vvw	1.838	41
				1.852	vvw	1.852	vvw	1.80	14
				1.743	w	1.743	w	1.805	w
				1.714	vvw	1.714	vvw	1.70	13
				1.611	vvw	1.611	vvw	1.61	14
				1.485	m, br	1.485	m, br	1.53	3
				1.492	m, br	1.495	m, br	1.47	2
				1.4332	19	1.4332	19	1.482	vvw
				1.316	vvw	1.315	vvw	1.41	10
				1.308	vw, br	1.308	vw, br	1.36	8
				1.202	vvw	1.202	vvw	1.310	20
				1.101	vvw, br	1.100	vvw, br	1.2582	8
				1.019	vvw, br	1.019	vvw, br	1.1885	7
				0.973	vw, br	0.975	vw, br	1.1620	10
				0.928	vvw, br	0.928	vvw, br	1.1405	11
				0.881	vw, br	0.881	vw, br	1.1024	13
				0.815	vvw, br	0.815	vvw, br	1.0551	17
				0.871	vvw, br	0.871	vvw, br	0.9890	9
				0.820	vvw, br	0.820	vvw, br	0.9601	18
				0.9064	12	0.9064	12	0.9578	12
				0.8275	6	0.8275	6	0.9512	11
				0.9152	w	0.9152	w	0.9080	24
				0.8330	w	0.8330	w		

The abbreviations for intensity values are: s, strong; m, medium; w, weak; vw, very weak; br, broad. Bulk material of all samples yielded identical diffraction photographs. Scrapings from sample nos. IIA, IIB and IIIB gave similar diffraction photographs. Taken from C. Aravindakshan and Sultana Z. Ali, J.S.I.R. 2/D (1962), 316; weak lines are omitted. Diffraction photograph was taken in a large camera of 114.6 mm dia.

iron ferrocyanide in addition to  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$ . The presence of iron ferrocyanide in the scrapings was confirmed by the following laboratory corrosion experiment.

A thoroughly filed and cleaned cut-piece from sample No. IV was hung in the regenerated ammoniacal liquor at about  $60^\circ\text{C}$ . Within a few min. after its immersion, a dark material, loose in texture, was formed on the walls of the experimental piece. A major portion of the dark material was detachable by shaking the specimen leaving a bright face. When the solution was changed to a fresh one, the same sort of dark material was again formed on the walls. The dark material imparted slowly a bluish colour to the solution. It was collected, dried at  $60^\circ\text{C}$  without washing and used for x-ray diffraction analysis in a sealed Lindemann glass capillary. The x-ray photograph showed that it was iron ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . However, when the experiment was repeated at room temperature, the rate of formation of the above type of dark material was very slow and its amount was negligible.

### Discussion and Conclusion

Spectroscopic analysis did not reveal appreciable differences in the bulk material of the samples. The elements usually found as traces in steel<sup>1</sup> were detected (Table 2).

The identification of  $\alpha\text{-Fe}$  in bulk material of all samples shows that the structure is ferritic and/or pearlitic. However, when the unit cell parameters of the body centered cubic structure of  $\alpha\text{-Fe}$  obtained from samples are calculated, the 'a' value is found to be slightly larger ( $a = 2.896 \text{ \AA}$ ) than the reported value, i.e.  $a = 2.866 \text{ \AA}$  for pure  $\alpha\text{-Fe}$ . This slight expansion in lattice is not surprising since ferrites are  $\alpha\text{-Fe}$  with carbon dissolved in their lattices.

It is well known that ammonia has only very little action on mild steel. But chemical analysis (Table 5) of the ammoniacal regenerated liquor indicates the association of other gases, viz. hydrogen sulphide, oxygen and carbon dioxide, etc., with it. These gases were found to have corrosion effect on mild steel singly or in combination with each other depending on the chemical environment of the system. Various types of iron sulphides formation by hydrogen sulphide have been reported<sup>2-4</sup> under different experimental conditions. Whitman et al<sup>5</sup> found that corrosion by oxygen was decreased in the alkaline medium, but the rate of corrosion was dependent of the rate of diffusion of oxygen. At ordinary temperatures carbon dioxide

exists as soluble ammonium carbonate and bicarbonate in the aqueous medium of ammonia, and as such it has practically no corrosive action on mild steel. But ammonium carbonate has a low decomposition temperature, and so a portion of it gets reconverted to carbon dioxide at higher temperatures; and this carbon dioxide in the wet condition influences the corrosive action due to hydrogen sulphide and oxygen. As a matter of fact, the presence of iron sulphides on the corroded surface of all samples was established by microscopic analysis, and that of magnetite and  $\alpha\text{-Fe}_2\text{O}_3$  by x-ray diffraction. All these products owe their origin to the corrosive action on mild steel by the dissolved gases like hydrogen sulphide, oxygen and carbon dioxide in the regenerated ammoniacal liquor.

TABLE 5—CHEMICAL ANALYSIS OF REGENERATED LIQUOR

No.	Constituents	Unit	Amount, %
1.	Total Ammonia	gms/lit	30–35
2.	$\text{CO}_2$	"	18–21
3.	$\text{H}_2\text{S}$	"	0.15–0.22
4.	HCN	"	0.002–0.006

A further examination of the chemical analysis (Table 5) shows the presence of a small amount of hydrocyanic acid. It is known that dry hydrocyanic acid has no reaction on mild steel. But, if corrosion is initiated by dissolved agents like hydrogen sulphide, oxygen, carbon dioxide and other impurities present in the regenerated liquor, it could be accelerated by dissolved hydrocyanic acid through a series of complex reactions, the end-product being iron ferrocyanide. Actually the latter has been detected in small amounts in some of the scrapings (Sample Nos. IA, IB & IV) as well as in the product obtained in the laboratory corrosion experiment carried out at  $60^\circ\text{--}65^\circ\text{C}$ .

The x-ray photographs of sample Nos. IIA, IIB & IIIA did not show any detectable amounts of iron ferrocyanide, because there was only very little formation of it due to the low temperature at the tube sides on account of the flow of the cooling water compared to the header and shell sides, through which warm regenerated liquor was sent. This is in agreement with the results of the corrosion experiment carried out at room temperature where the formation of iron ferrocyanide was very slow and much less. Thus, corrosion by dissolved hydrocyanic acid also takes place in the coolers mainly on the warmer portions. This is substantiated also by the fact that a blue coloured

product is found to be formed over the shell sides wherever the warm regenerated liquor is flowing.

It is therefore clear that corrosion of mild steel by regenerated ammoniacal liquor in the coolers has been mainly due to the chemical impurities like hydrogen sulphide, hydrocyanic acid, carbon dioxide and oxygen, etc. dissolved in it. As the chemical reactions are normally accelerated at higher temperatures, corrosion takes place at a faster rate on the coolers through which warm regenerated liquor is sent. This kind of attack becomes preferential at the welded regions due to the reduction of grain size, precipitation of trace elements, formation of holes and crannies during heat treatment and cooling, as well as the welding defects such as non-alignment of edges, badly fitted parts, incorrectly prepared joints, poorly fused areas, lack of penetration, slag inclusion, etc.

The corrosion products, thus formed, are removed continuously by the flowing fluid, and corrosion on the surface of the metal continues indefinitely, resulting in large scale pitting and cracking. So, it is considered that the removal of impurities like hydrogen sulphide

and hydrocyanic acid from coke oven gas is necessary to minimise failures due to corrosion on mild steel equipment.

#### Acknowledgments

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## Evaluation of Some Primers by Laboratory Tests

By

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Single and double coats of three primers—zinc chromate, zinc based and composite red oxide-aluminium-zinc chromate—were applied on mild steel panels and their performance was assessed by the immersion and scratch evaluation tests in three per cent solutions of sodium chloride, ammonium sulphate, ammonium sulphate-nitrate and urea. These tests indicated that the composite primer red oxide-aluminium-zinc chromate was markedly superior to the other two primers, and this result seems to correlate with the resistance measurements of the coated panels in three per cent solutions of sodium chloride and ammonium sulphate.

Carbon Steel structures and equipment have been found to undergo severe corrosion in fertilizer plants. To minimise it, large quantities of paints are used; but experience has shown that many primers and top coats, which have given excellent service elsewhere, have failed within a short time in the fertilizer factory area. The reason is that environment and

conditions vary in different industries and even in the different areas of the same plant.

The present investigation was undertaken to study the performance of different primers and topcoats in fertilizer plants and also to evolve reliable accelerated tests for this purpose. In the first phase of this work, single and double coats of three commercial primers

were applied on mild steel panels which were then immersed at constant temperature in 3 per cent solutions of three different fertilizers, namely, urea, ammonium sulphate and ammonium sulphate nitrate and also in 3 per cent solution of sodium chloride. In some experiments, scratches to bare metal were made on the panels before immersing them in the solutions. The panels were examined after definite intervals to determine the extent of damage. Such tests have been carried out by other investigators to assess the chemical resistance of primers and topcoats<sup>1-3</sup>.

Resistance measurements were also carried out with the coated panels immersed in salt solutions. These measurements have been shown by some workers<sup>4, 5</sup> to give an indication of the performance of protective coatings in contact with salt solutions—a higher resistance value signifying, in general, a greater stability of the coating.

### Experimental Procedure

**Materials:** The following three primers were procured for the present study: zinc based, zinc chromate

and the red oxide—aluminium-zinc chromate composite primer. The vehicle for all the three primers was linseed alkyd according to the information supplied by the suppliers.

**Preparation of Coated Panels:** Test panels 3"×6" were prepared from M. S. sheet 1/8" thick. The surfaces of the panels were prepared by emery paper after they were cleaned thoroughly and degreased. One set of panels was then phosphate-treated<sup>6</sup> and one and two coats of primers were applied on both sides of them by brushing. Another set of panels was coated similarly without any pretreatment. The dry film thickness of the coated panels was measured by a magnetic thickness gauge. The average values are shown below:

Primers	Film thickness, mil.	
	on single coat	on double coat
Zinc Based .. .. .	2.0	3.5
Zinc Chromate .. .. .	2.0	4.0
Red Oxide-Aluminium—Zinc Chromate	1.5	2.0

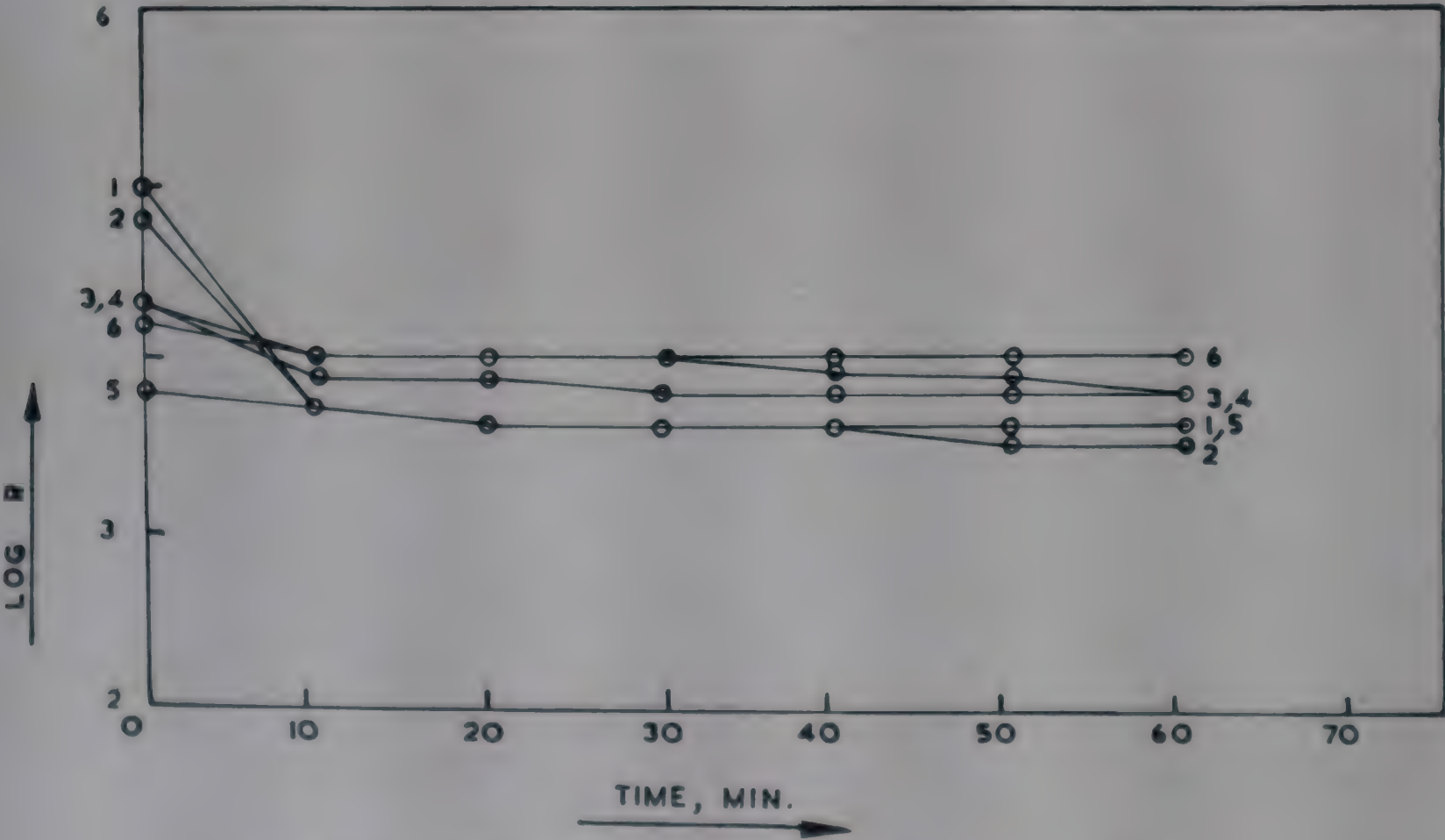


Fig. 1. Resistance Measurements of Coated Panels in Sodium Chloride Solution.

1. Zinc Based Primer on Treated Panel.

2. Zinc Chromate Primer on Treated Panel.
3. Red Oxide-Zinc Chromate Primer on Treated Panel.

4. Zinc Based Primer on Untreated Panel.
5. Zinc Chromate Primer on Untreated Panel.

6. Red Oxide, Zinc Chromate Primer on Untreated Panel.

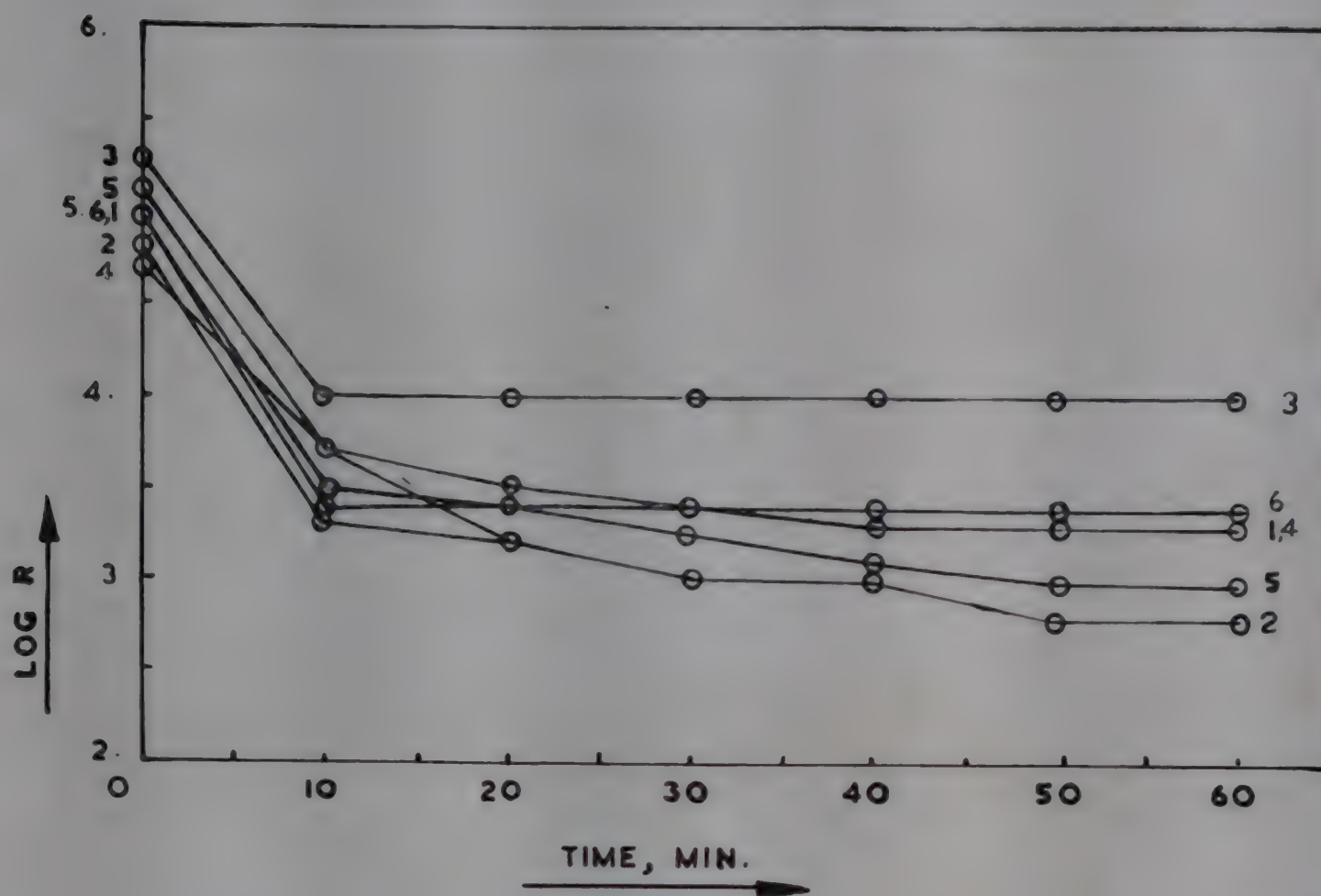


Fig. 2. Resistance Measurements of Coated Panels in Ammonium Sulphate Solution.

- |   |   |   |
|---|---|---|
| 1. Zinc Based Primer on Treated Panel.    | 3. Red Oxide/Zinc Chromate Primer on Treated Panel. | 5. Zinc Chromate Primer on Untreated Panel.           |
| 2. Zinc Chromate Primer on Treated Panel. | 4. Zinc Based Primer on Untreated Panel.            | 6. Red Oxide/Zinc Chromate Primer on Untreated Panel. |

**Immersion and Scratch Evaluation Tests:** In the scratch evaluation test, scratches (25 mm.  $\times$  1 mm.) were made on the coated panels which were then kept completely immersed at 30°C in separate glass beakers containing 3 per cent solutions of sodium chloride, ammonium sulphate, urea and ammonium sulphate-nitrate. The signs of corrosion and blistering, in and around the scribe mark and away from it, were noted in the different cases after suitable intervals up to a total period of two weeks, and from these observations the relative evaluation of the primers was made. The results are given in Table 1.

In separate series of experiments panels with single and double coats of primers were kept immersed at 30°C in the same solutions as described above but without any scribe marks on them. At suitable intervals, observations were made for the first appearance of blisters, signs of corrosion, loss of adhesion and underfilm damage, and then a comparative evaluation was made (Tables 2 & 3).

**Resistance Measurements:** Resistance measurements were made in 3 per cent solutions of sodium chloride

and ammonium sulphate at 30°C. The portion of the panel above the liquid and up to some portion well inside it was coated with paraffin wax. The surface area of the immersed portion of the specimen not protected by paraffin was 49 sq. cm. The resistance values of the coated panels were measured by a vacuum tube ohmmeter using a platinum electrode. The first reading was taken within one minute after immersion and thereafter at intervals of 10 minutes up to a total period of 1 hour. The logarithms of resistance (in ohms) were plotted against time (Figs. 1 & 2).

### Results and Discussion

The visual observations in the scratch evaluation and immersion tests (Tables 1-3) indicate that the composite red oxide-aluminium-zinc chromate primer is the best among the three samples studied, as regards the performance in solutions of the fertilizers and sodium chloride. The phosphate-treated panels, in general, showed better performance than the untreated ones. The performance of zinc-based primer was not so good as that of red oxide-aluminium-zinc chromate while

TABLE 1—SCRATCH EVALUATION TESTS IN DIFFERENT SOLUTIONS  
(Single Coat of Primer Applied)

Primer Sample	Duration of test, hr.	Common Salt		Ammonium Sulphate		Ammonium Sulphate-Nitrate		Urea	
		Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated
Zinc Inorganic	168	The scratch line has widened up to 2 mm, with sign of corrosion. No corrosion below the line under the film.	Widening of the scribe mark to more than 3 mm with deepening of the scratch line. Corrosion under the film. Discontinued after 144 hr.	Very little change. Slight deepening of the scratch line. No corrosion below the line.	Widening of the scribe mark to more than 3 mm, with deepening of the scratch; under film corrosion. Discontinued after 144 hr.	Slight deepening of the scratch line. Very little sign of corrosion beyond the scratch line under the film.	Deepening of the scratch with spreading corrosion under the film.	Very little change. No spreading.	Very little change.
Zinc Chromate	168	Widening of the scribe mark to 3 mm with deepening. Corrosion under the film. Discontinued after 120 hr.	Widening of the scratch line to more than 3 mm with deepening. Corrosion under the film. Discontinued after 120 hr.	Widening and deepening of the scribe mark to about 2 mm. Slight corrosion under the film.	Widening of scribe mark to more than 3 mm with deepening and under film corrosion. Discontinued after 120 hr.	Widening and deepening of the scribe mark to more than 3 mm with corrosion under the film. Discontinued after 120 hr.	Widening of the scribe mark to more than 3 mm with deepening corrosion under the film. Discontinued after 120 hr.	No change.	Very little change
Red Oxide	168	Very little change.	Slight widening of the scribe mark. Slight corrosion under the film.	Very little change.	Widening and deepening of the scribe mark. Sign of corrosion under the film.	Widening of the scribe mark to about 2 mm. Very little corrosion under the film.	Widening of scribe mark with deepening of the line to about 4 mm. Under-film corrosion.	No appreciable change	Very little change

TABLE 2.—IMMERSION TESTS IN DIFFERENT SOLUTIONS

(Single Coat of Primer Applied)

Primer Sample	Duration of test, hr.	Common Salt		Ammonium Sulphate		Ammonium Sulphate-Nitrate		Urea	
		Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated
Zinc Inorganic	168	Small few blisters with brown spots at places after 144 hr.	Blistering after 48 hr. Swelling of film throughout the panel; rust under the film. Discontinued.	Small blisters over the panel after 144 hr.	Moderate blisters throughout the panel after 48 hr.	Few brown spots here and there with small blisters after 120 hr.	Minute blisters throughout the panel with one or two brown spots after 48 hr.	No change.	Rust spots at places after 48 hr.
	336	The earlier effect becomes more pronounced. Pin-point rust under the film at places.	—	Only a few brown spots at places; rust under the film at places.	Severe rusting at the place of blisters and other places; discontinued after 192 hr.	The earlier effect becomes more pronounced with sign of corrosion under the film.	The effect becomes more pronounced with more signs of corrosion after 288 hr. Discontinued.	No appreciable change.	The effect becomes more pronounced; sign of corrosion.
Zinc Chromate	168	Moderate size blisters throughout the panel with brown spots after 72 hr.	Dense rust throughout the panel. Discontinued after 144 hr.	Small blisters and brown spots at places of blisters after 72 hr.	Blisters at some places after 24 hr. and with rust spot at places after 48 hr.	Sign of severe corrosion throughout the panel after 144 hr. Discontinued.	Sign of corrosion at the place of blisters and throughout the panel. Discontinued after 120 hr.	Very minute brown spots throughout the panel after 120 hr.	Sporadic rust spots throughout the panel by 144 hr.
	336	Rusting at the place of blisters; sign of corrosion under the film.	—	The earlier effect becomes more throughout the panel.	Rusting throughout the panel after 192 hours.	—	—	The earlier effect becomes more pronounced with sign of corrosion under the film.	—
Red Oxide	168	Minute blisters packed at one place after 96 hr.	Minute dense blisters throughout the panel after 48 hr.	No change.	Small dense blisters throughout the panel after 72 hr.	No appreciable change.	Small dense blisters throughout the panel.	Nothing Noticeable.	A few minute blisters at places.
	336	Condition remains almost same; Pin point corrosion under the film at places.	The earlier effect becomes more pronounced with signs of corrosion at the place of blisters after 288 hr. Discontinued.	Some small blisters over the panel.	The effect becomes more pronounced with sign of corrosion at the place of blisters after 288 hr. Discontinued.	A few small blisters at places.	Sign of corrosion in $\frac{1}{4}$ portion of the panel after 244 hr. Discontinued.	No appreciable change.	Sign of rust at the place of blisters after 288 hr. Discontinued

# Agronomical Significance of Carbon Nutrition

## Part II—Studies on the Efficiency of Various Forms of Ammoniacal Nitrogen:

### RESPONSE OF *AUS* PADDY IN POT CULTURE\*

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The behaviour and relative efficiencies of four different nitrogenous compounds, viz. ammonium bicarbonate, ammonium carbonate, ammonium sulphate and ammonia, have been studied under dry as well as water-logged conditions. The effect and the interaction of the different anions such as  $(\text{CO}_3)''$ ,  $(\text{HCO}_3)'$ ,  $(\text{SO}_4)''$  and  $(\text{OH})'$  on plant growth in presence of ammonium nitrogen have also been studied under the same conditions.

While ammonium bicarbonate has proved the most efficient source in encouraging vegetative as well as reproductive growth under dry condition, under water-logged condition ammonium carbonate proved the best. Ammonium sulphate, on the other hand, proved inferior to both ammonium carbonate and bicarbonate. The yield of dry rice tops was significantly higher than of the water-logged rice tops, whereas the reverse was true in the case of the roots. Water-logged rice plants take up significantly larger amounts of phosphate than the corresponding dry plants. Water-logged rice roots have been found to have 40 per cent less carbon than the corresponding dry roots, indicating the significance of carbon nutrition through roots under normal aerobic conditions.

#### Introduction

The Food and Agriculture Organisation (F.A.O.) of the United Nations established in 1947 a subsidiary group known as the International Rice Commission, for coordinating the activities of the governments concerned in regard to the production and distribution of rice. The results presented at fourth meeting<sup>1-3</sup> of this Commission confirmed that nitrogen is the plant nutrient element which is most needed in many countries to increase the yield of rice.

In this investigation\*, the relative efficiencies of ammonium carbonate, ammonium bicarbonate, ammonium sulphate and ammonia as nitrogenous sources have been studied under dry as well as water-logged conditions. The study of the effect of carbon

nutrition under the above two conditions was also made possible here.

#### EXPERIMENTAL

##### Analytical Methods

*Microdigestion of the Plant Material:* For the determination of nitrogen, phosphorus and potassium in the plant material, the microdigestion method of Yuen and Pollard<sup>4</sup> was followed.

Ammoniacal nitrogen in the fertilizers was determined by the microdistillation method using the Markham still, while the ammonia nitrogen in the plants by the modified Nessler's method<sup>5</sup>. The phosphate in the plants was determined by the molybdenum blue-amino-naphthol sulphonic acid method<sup>6</sup>, potassium by the photometric and the organic carbon by Walkley and Black's method<sup>7</sup> using a powerful light for titration. It was observed that the last method<sup>7</sup> gives results comparable to those by any other standard method. Critical samples were checked by Van Slyke-Folch's method.

\* This investigation was carried out by the author at the Imperial College of Science & Technology, London.

*Editor's Note:* This investigation together with its follow-up, carried out in field experiments and appearing elsewhere in this issue (pp. 48-52), form the background of the work being pursued by the author in this Division of FCI Ltd. In a forthcoming issue of TECHNOLOGY the results obtained by him in this laboratory will be published.

## Pot Culture Method

(a) *Description of the Soil:* A neutral loam (pH 6.9) from Harlington (London) was dried, and passed through a 2 mm. sieve before potting (Table 1). Earthen pots, coated with black bitumen paint, holding 1 Kg. of soil were used.

TABLE 1—ANALYTICAL DATA FOR THE SOIL USED

(Expressed on oven dry basis)

Determination of	Method	Result
Total N, %	Kjeldahl	0.156
Total P <sub>2</sub> O <sub>5</sub> %	Boiling Hcl	0.220
Total K %	Boiling Hcl	0.345
Total NH <sub>4</sub> ppm	Morgan Extract	8.5
Total P <sub>2</sub> O <sub>5</sub> ppm	Morgan Extract	221.0
Total K ppm	Morgan Extract	163.0
Total Exchangeable bases m.e./100g. soil	Ammonium Acetate	10.09
Cation Exchange Capacity	Ammonium Acetate	11.86
Organic Carbon, %	(Walkley & Black)	1.9
Water holding Capacity, %	—	43
Mechanical analysis	(Hydrometer)	
Sand, %	—	52.0
Silt, %	—	24.6
Clay, %	—	18.7

(b) *Test Crop:* The Jhanji-35 variety of *Aus* paddy, normally grown under dry conditions in W. Bengal, was selected, because it also gives good performance even in fields water-logged very often due to heavy rains.

(c) *Fertilizers Used:* Ammonium carbonate, ammonium bicarbonate, ammonium sulphate and ammonia were used at three levels viz. 50, 100 and 200 lbs. of nitrogen per acre.

(d) *Statistical Design for the Experiment:* Randomised block design with 2 replicates for each set.

*Experimental Procedure:* The pots were first lined with polythene sheeting and 1 Kg of the sieved soil was then weighed into each pot. Treatments within each block were randomised individually. There were altogether 78 pots in this experiment, each block containing 13 pots.

*Sowing:* On 8.4.60, 10 seeds sown in each pot with the ultimate object of keeping 4 plants per pot. Just after sowing, all the pots were irrigated with 200 ml. of distilled water. Germination was completed by 25.4.60, and on the same date the seedlings were thinned down to 4 per pot.

*Application of the Fertilizers:* All the fertilizers were

applied in solution. The half of the total nitrogen was applied at the tillering stage while the remainder one month later. In the water-logged pots, before each application of the fertilizer, the supernatant liquid was allowed to dry off and immediately after the application they were water-logged again.

The total nitrogen applied was as follows:

Abbreviations	N-Fertilizers	Lbs N/Acre	Mg. N/Pot
Control	0	0	0
C <sub>1</sub>	Ammonium Carbonate	50	25
C <sub>2</sub>	Ammonium Carbonate	100	50
C <sub>3</sub>	Ammonium Carbonate	200	100
S <sub>1</sub>	Ammonium Sulphate	50	25
S <sub>2</sub>	Ammonium Sulphate	100	50
S <sub>3</sub>	Ammonium Sulphate	200	100
A <sub>1</sub>	Ammonia	50	25
A <sub>2</sub>	Ammonia	100	50
A <sub>3</sub>	Ammonia	200	100
B <sub>1</sub>	Ammonium Bicarbonate	50	25
B <sub>2</sub>	Ammonium Bicarbonate	100	50
B <sub>3</sub>	Ammonium Bicarbonate	200	100

After each week, blocks were rotated and interchanged amongst themselves, keeping the randomisation within each block intact, to ensure equal light and temperature to all the pots. The greenhouse was maintained at 70°-80°F, which is considered optimum for the vigorous vegetative growth of this particular variety of rice.

*Irrigation:* In the dry pots, 10 ml. of distilled water was applied every day, while in the water-logged ones the loss of the supernatant liquid was made up every day by adding the same quantity of water.

## RESULTS

In the water-logged set, the morphological differences due to the different treatments were recognized in about a fortnight after the first application of the fertilizers. The differences were considerable only in those pots receiving the third-level treatments. The C<sub>3</sub> and B<sub>3</sub>—treated plants had more tillers, broader deep-green leaves and stouter appearances than the corresponding S<sub>3</sub> and A<sub>3</sub> plants. In the dry set, the same trend was noticed, but the differences between the different treatments were smaller (Figs. 1 & 2).

Differences due to the different fertilizer treatments became very noticeable a month after the second application. Ammonium bicarbonate and ammonium carbonate plants had significantly more tillers, stouter stems and larger leaves than the corresponding ammo-

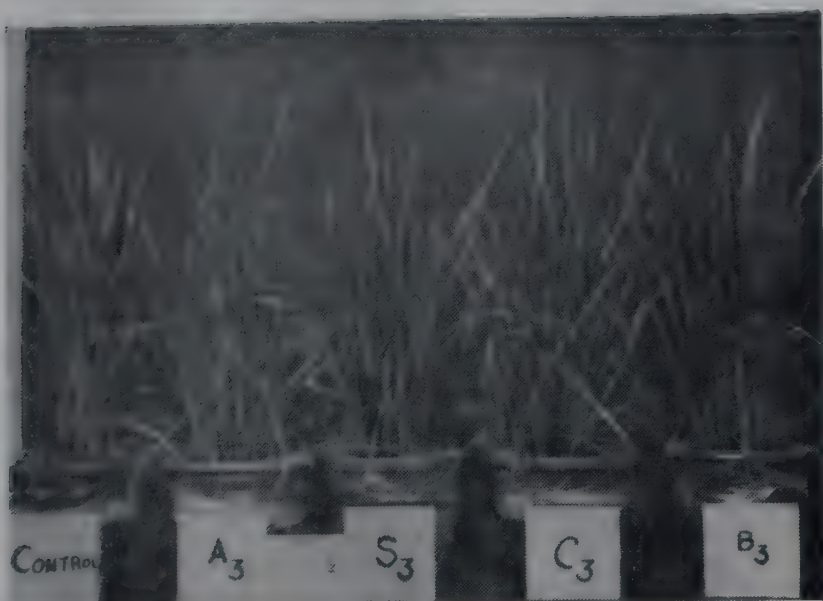


Fig. 1. Effect of Fertilizers on the Vegetative Growth (Dry Rice Plants).  
Treatments: Control A<sub>3</sub> S<sub>3</sub> C<sub>3</sub> B<sub>3</sub>  
[Photo taken fortnight after the final application of fertilizers]

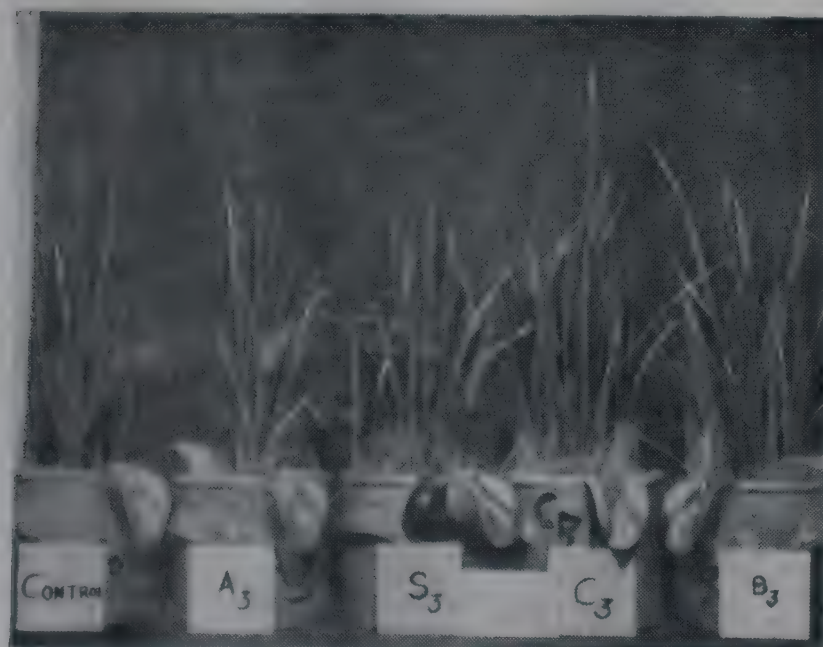


Fig. 2. Effect of Fertilizers on the Vegetative Growth. Water-logged Rice Plant.  
Treatments: Control A<sub>3</sub> S<sub>3</sub> C<sub>3</sub> B<sub>3</sub>

nium sulphate, and ammonia-treated plants at all three levels of nitrogen application. These differences were much more evident in the water-logged set than in the corresponding dry set. This was probably due to the "ammophile" nature<sup>8</sup> of the rice plants. In general, the water-logged plants were yellowish in appearance as compared with the deep green appearance of the dry rice plants. Vegetative growth appeared to be more vigorous in the dry rice tops.

**Harvesting:** In order to determine the dry matter yield and the nutrient status of the rice plants at the peak period of their vegetative growth, blocks 1 and 2 of both sets (dry and water-logged) were harvested. The tops and roots were separated, dried, weighed and analysed.

**Dry Matter Yields of the Rice Plants:** At 5 per cent level of significance, the statistical interpretation of the results is as follows:

(a) Dry Rice Tops (Table 2, column 2)

\* B<sub>3</sub> C<sub>3</sub> S<sub>3</sub> C<sub>2</sub> B<sub>2</sub> A<sub>3</sub> S<sub>2</sub> C<sub>1</sub> B<sub>1</sub> A<sub>2</sub> A<sub>1</sub> S<sub>1</sub> Control

(b) Water-logged Rice Tops (Table 2, column 3)

C<sub>3</sub> B<sub>3</sub> S<sub>3</sub> C<sub>2</sub> B<sub>2</sub> S<sub>2</sub> A<sub>3</sub> B<sub>1</sub> C<sub>1</sub> A<sub>2</sub> S<sub>1</sub> A<sub>1</sub> Control

The yields of the dry rice tops were significantly higher than those of the water-logged rice tops. The difference between the different treatments, however, were definitely wider in the water-logged plants. This is confirmed by the higher F value (62.48) of the water-logged rice tops as compared with 43.32 for the dry-rice tops. Within the third-level treatments, B<sub>3</sub> proved superior to C<sub>3</sub> in producing top yields under dry condition whereas the reverse was true under water-logged condition. This was probably due to the aerobic nature of carbon dioxide fixation by the roots.

(c) Dry Rice Roots (Table 2, column 4)

S<sub>3</sub> B<sub>3</sub> A<sub>3</sub> S<sub>2</sub> C<sub>3</sub> C<sub>2</sub> A<sub>2</sub> A<sub>1</sub> B<sub>2</sub> Control S<sub>1</sub> C<sub>1</sub> B<sub>1</sub>

(d) Water-logged Rice Roots (Table 2, column 5)

S<sub>3</sub> B<sub>3</sub> C<sub>3</sub> A<sub>3</sub> S<sub>2</sub> C<sub>2</sub> A<sub>1</sub> A<sub>2</sub> S<sub>1</sub> Control C<sub>1</sub> B<sub>2</sub> B<sub>1</sub>

The yield of roots under water-logged condition was significantly higher than that under dry condition. The water-logged roots were thicker and yellowish in appearance, whereas the corresponding dry roots were thinner and whitish.

(a) *Nitrogen in the Dry Rice Tops* (Table 3, column 3)

In general, the percentage of nitrogen in the rice tops increased with the amount of nitrogen applied. Within the third-level treatments, the order of the percentage of nitrogen in the tops was B<sub>3</sub>=S<sub>3</sub> > C<sub>3</sub> > A<sub>3</sub>. At the second level, it was A<sub>2</sub> > B<sub>2</sub> > S<sub>2</sub> > C<sub>2</sub> and at the first it was A<sub>1</sub> > S<sub>1</sub> > C<sub>1</sub>=B<sub>1</sub>.

\* (1) Treatments are arranged in order of their respective merit.

(2) Treatments within the same bar indicate that the observed differences between the treatments are due to chance.

TABLE 2—EFFECT OF VARIOUS AMMONIACAL NITROGENOUS MATERIALS ON THE DRY MATTER YIELD OF RICE TOPS AND ROOTS

(Each figure represents an average of two blocks)

Treatments	Yield of dry-rice tops, g.	Yield of water-logged rice tops, g.	Yield of dry-rice roots, g.	Yield of water-logged rice roots, g.
Control	4.92	3.63	4.99	7.48
C <sub>1</sub>	7.34	5.11	4.57	7.43
C <sub>2</sub>	8.83	7.44	5.93	8.69
C <sub>3</sub>	10.68	10.63	5.95	10.49
S <sub>1</sub>	5.58	4.14	4.75	7.62
S <sub>2</sub>	7.69	6.21	6.54	9.37
S <sub>3</sub>	9.91	9.15	8.52	11.30
A <sub>1</sub>	5.63	4.00	5.33	8.54
A <sub>2</sub>	6.24	4.65	5.79	8.13
A <sub>3</sub>	7.85	5.97	6.67	10.25
B <sub>1</sub>	7.16	5.31	4.37	6.20
B <sub>2</sub>	8.24	6.73	5.32	7.15
B <sub>3</sub>	11.68	9.52	6.90	11.24
F value of the treatments	43.22***	62.48***	9.54***	2.32
F value of the blocks	2.60	1.49	3.38	5.19*
C.D. at the 5% level	0.397	0.358	0.465	1.357

\* Significant at the 5% level.

\*\* Significant at the 1% level.

\*\*\* Significant at the 0.1% level.

C.D. = Critical difference.

"F" Value = Variance ratio value.

TABLE 3—PERCENTAGE OF CARBON, NITROGEN, PHOSPHATE (P<sub>2</sub>O<sub>5</sub>) & POTASSIUM IN DRY RICE TOPS

Treatments	Carbon	Nitrogen	Phosphate	Potassium
Control	36.3	.38	.55	1.67
C <sub>1</sub>	38.0	.41	.46	1.70
C <sub>2</sub>	37.1	.42	.50	1.75
C <sub>3</sub>	37.2	.52	.46	1.70
S <sub>1</sub>	36.2	.42	.60	1.95
S <sub>2</sub>	36.9	.50	.46	1.77
S <sub>3</sub>	37.1	.58	.41	1.70
A <sub>1</sub>	36.2	.47	.50	1.70
A <sub>2</sub>	36.9	.58	.41	1.60
A <sub>3</sub>	36.8	.50	.46	1.70
B <sub>1</sub>	37.1	.41	.55	1.77
B <sub>2</sub>	35.6	.56	.46	1.85
B <sub>3</sub>	37.2	.58	.46	1.82

(b) Nitrogen in the Water-logged Rice Tops (Table 4, column 3)

In this case also, the percentage of nitrogen in the tops increased with the amounts applied. Within the third-level treatments, the order of the percentage of nitrogen in the tops was A<sub>3</sub>=C<sub>3</sub> > S<sub>3</sub> > B<sub>3</sub>. At the second-level it was A<sub>2</sub> > C<sub>2</sub> > S<sub>2</sub> > B<sub>2</sub> and at the first-level it was A<sub>1</sub> > C<sub>1</sub>=B<sub>1</sub>=S<sub>1</sub>.

The percentage of nitrogen in the rice tops was not affected by water-logging, as both the dry and the water-logged rice tops had similar values for the corresponding treatments. However, water-logging resulted in lower values in the ammonium bicarbonate treated tops at all the three levels than the corresponding ammonium carbonate, ammonium sulphate and ammonia-treated tops. Ammonia treatment resulted in the highest percentage of nitrogen in the rice tops at all the three levels under dry (except A<sub>3</sub>) as well as water-logged conditions.

TABLE 4—PERCENTAGE OF CARBON, NITROGEN, PHOSPHATE (P<sub>2</sub>O<sub>5</sub>) & POTASSIUM IN WATER-LOGGED RICE TOPS

Treatments	Carbon	Nitrogen	Phosphate	Potassium
Control	35.5	.41	.50	1.80
C <sub>1</sub>	35.7	.42	.60	1.80
C <sub>2</sub>	37.3	.48	.60	1.92
C <sub>3</sub>	37.1	.52	.60	1.70
S <sub>1</sub>	36.2	.42	.60	1.85
S <sub>2</sub>	36.2	.47	.55	1.85
S <sub>3</sub>	35.4	.51	.50	1.82
A <sub>1</sub>	35.2	.45	.60	1.75
A <sub>2</sub>	35.1	.57	.55	1.80
A <sub>3</sub>	34.7	.52	.55	1.75
B <sub>1</sub>	35.7	.42	.62	1.75
B <sub>2</sub>	35.6	.42	.60	1.70
B <sub>3</sub>	36.2	.43	.60	1.67

(c) Total Nitrogen Uptake of the Rice Tops

At 5 per cent level of significance, the statistical interpretation of the results is as follows:

(i) Dry rice Tops (Table 7, column 2)

B<sub>3</sub> S<sub>3</sub> C<sub>3</sub> B<sub>2</sub> A<sub>3</sub> S<sub>2</sub> C<sub>2</sub> A<sub>2</sub> C<sub>1</sub> B<sub>1</sub> A<sub>1</sub> S<sub>1</sub> Control

(ii) Water-logged Rice Tops (Table 7, column 3)

C<sub>3</sub> S<sub>3</sub> B<sub>3</sub> C<sub>2</sub> A<sub>3</sub> S<sub>2</sub> B<sub>2</sub> A<sub>2</sub> B<sub>1</sub> C<sub>1</sub> A<sub>1</sub> S<sub>1</sub> Control

Under dry condition, at all the three levels of nitrogen application, ammonium bicarbonate-treated tops took up significantly more N than did the corresponding ammonium carbonate-treated tops, whereas, under water-logged condition, the relationship was reversed.

(d) *Nitrogen in the Dry Rice Roots* (Table 5, column 3)

The percentage of nitrogen in the roots increased with increasing amounts of nitrogen applied. At the third-level, the order of the percentage of nitrogen of the roots was  $B_3 > C_3 > S_3 > A_3$ . At the second-level, it was  $B_2 > C_2 = A_2 > S_2$  and at the first-level it was  $B_1 > C_1 > S_1 > A_1$ .

(e) *Nitrogen in the Water-logged Rice Roots* (Table 6, column 3)

In this case also, the percentage of nitrogen in the roots increased with increasing amounts of N application. At the third-level, the order of the percentage of nitrogen in the roots was  $A_3 = C_3 > B_3 = S_3$ , at the second-level, it was  $A_2 > B_2 > C_2 > S_2$  and at the first-level all of them had the same value.

Under the dry condition, ammonium bicarbonate at all the three levels, produced the highest percentage of nitrogen in the roots, whereas under water-logged condition, ammonia treatment at all the three levels of nitrogen resulted in the higher values than the corresponding ammonium bicarbonate, ammonium carbonate and ammonium sulphate treatments.

(f) *Total N Uptake of the Roots:*

At 5 per cent level of significance, the interpretation of the results is as follows:

(i) *Dry-rice Roots* (Table 7, column 4)

$S_3 \ B_3 \ C_3 \ A_3 \ S_2 \ C_2 \ A_2 \ B_2 \ A_1 \ B_1 \ C_1 \ S_1 \ \text{Control}$

(ii) *Water-logged rice roots* (Table 7, column 5)

$S_3 \ B_3 \ C_3 \ A_3 \ A_2 \ C_2 \ S_2 \ B_2 \ A_1 \ S_1 \ C_1 \ \text{Control} \ B_1$

(g) *Total Nitrogen Uptake of the Whole Rice Plants:*

At 5 per cent level of significance, the statistical interpretation of the results is as follows:

(i) *Dry-rice Plants* (Table 7, column 6)

$B_3 \ S_3 \ C_3 \ B_2 \ A_3 \ S_2 \ C_2 \ A_2 \ C_1 \ B_1 \ A_1 \ S_1 \ \text{Control}$

(ii) *Water-logged Rice Plants* (Table 7, column 7)

$C_3 \ S_3 \ B_3 \ A_3 \ C_2 \ S_2 \ A_2 \ B_2 \ C_1 \ A_1 \ B_1 \ S_1 \ \text{Control}$

Under dry condition, ammonium bicarbonate resulted in the highest nitrogen uptake at all three levels of nitrogen application, whereas, under water-logged condition, ammonium carbonate caused the highest uptake of nitrogen.

**Proportion of Fertilizer N Taken Up**

In the different fertilizer treatments, the utilization of the nitrogen actually supplied was calculated by compensating for the uptake of nitrogen by the control plants.

**Dry Rice Plants**

(1)  $B_3$ -treated plants utilized 64 per cent of the total nitrogen supplied, whereas,  $S_3$ ,  $C_3$  and  $A_3$  plants utilized 58, 48 and 31 per cent respectively.

(2)  $B_2$  plants utilized 81 per cent whereas,  $S_2$ ,  $C_2$  and  $A_2$  plants utilized 59, 54 and 51 per cent respectively of nitrogen supplied to them.

(3)  $B_1$  plants utilized 54 per cent of the total nitrogen supplied, whereas,  $C_1$ ,  $A_1$  and  $S_1$  plants utilized 56, 44 and 27 per cent respectively.

At all the three levels, ammonium bicarbonate treatment resulted in the highest utilization of nitrogen as compared with the corresponding ammonium carbonate, ammonium sulphate and ammonia treatments. Maximum utilization of nitrogen was noticed at the second level of application.

**Water-logged Rice Plants**

(1)  $C_3$  plants utilized 58 per cent of the total nitrogen supplied, whereas,  $S_3$ ,  $B_3$  and  $A_3$  plants utilized 50, 45 and 33 per cent respectively.

(2)  $C_2$  plants utilized 54 per cent, whereas,  $S_2$ ,  $A_2$ ,  $B_2$  plants utilized 41, 40 and 35 per cent respectively of nitrogen supplied to them.

(3)  $C_1$  plants utilized 32 per cent of the total nitrogen supplied, whereas,  $A_1$ ,  $B_1$  and  $S_1$  plants utilized 26, 25 and 17 per cent respectively.

Unlike the dry rice cultures, in this case, maximum utilization of nitrogen occurred at the third levels of nitrogen application.

From the above results it can be concluded that in general the dry-rice plants utilized more nitrogen than the corresponding water-logged plants.

TABLE 5—PERCENTAGE OF CARBON, NITROGEN, PHOSPHATE &amp; POTASSIUM IN DRY RICE ROOTS

Treatments	Carbon	Nitrogen	Potassium	Phosphate ( $P_2O_5$ )
Control	34.1	.25	1.21	.38
C <sub>1</sub>	36.0	.34	1.26	.30
C <sub>2</sub>	34.1	.36	1.15	.30
C <sub>3</sub>	34.0	.41	1.11	.31
S <sub>1</sub>	33.8	.31	1.25	.38
S <sub>2</sub>	34.0	.35	1.50	.37
S <sub>3</sub>	33.7	.37	1.52	.37
A <sub>1</sub>	34.0	.30	1.37	.38
A <sub>2</sub>	33.9	.36	1.43	.38
A <sub>3</sub>	33.8	.36	1.33	.38
B <sub>1</sub>	36.2	.36	1.30	.37
B <sub>2</sub>	35.0	.38	1.28	.34
B <sub>3</sub>	36.2	.40	1.33	.34

TABLE 6—PERCENTAGE OF CARBON, NITROGEN, PHOSPHATE &amp; POTASSIUM IN WATER-LOGGED RICE ROOTS

Treatments	Carbon	Nitrogen	Potassium	Phosphate ( $P_2O_5$ )
Control	24.9	.19	.83	.53
C <sub>1</sub>	25.8	.21	.82	.53
C <sub>2</sub>	26.7	.23	.78	.60
C <sub>3</sub>	26.7	.30	.70	.67
S <sub>1</sub>	25.1	.21	1.00	.58
S <sub>2</sub>	26.1	.21	.95	.48
S <sub>3</sub>	26.0	.29	1.03	.53
A <sub>1</sub>	25.5	.21	.95	.58
A <sub>2</sub>	25.4	.28	1.07	.64
A <sub>3</sub>	25.5	.30	.98	.67
B <sub>1</sub>	27.0	.21	.86	.53
B <sub>2</sub>	28.8	.26	.91	.62
B <sub>3</sub>	25.5	.29	.82	.62

TABLE 7—EFFECTS OF FERTILIZERS ON THE UPTAKE OF NITROGEN BY RICE

(Figures expressed in mg.)

(Each figure represents an average of two blocks)

Treatments	Dry Rice Tops	Water-logged Rice Tops	Dry Rice Roots	Water-logged Rice Roots	Total Uptake of the Whole Dry Rice Plants	Total Uptake of the Whole Water-logged Plants
Control	19.10	14.98	12.79	14.43	31.89	29.42
C <sub>1</sub>	30.24	21.73	15.70	15.76	45.95	37.49
C <sub>2</sub>	37.55	36.23	21.47	20.60	59.03	56.83
C <sub>3</sub>	56.10	55.84	24.54	32.11	80.64	87.95
S <sub>1</sub>	23.74	17.62	15.13	16.15	38.87	33.78
S <sub>2</sub>	38.48	29.54	23.28	20.44	61.77	49.98
S <sub>3</sub>	58.22	46.86	31.96	33.11	90.19	79.97
A <sub>1</sub>	26.75	18.03	16.30	18.10	43.06	36.13
A <sub>2</sub>	36.68	26.73	20.96	22.84	57.64	49.58
A <sub>3</sub>	39.28	31.38	24.16	31.36	63.45	62.75
B <sub>1</sub>	29.52	22.59	16.11	13.15	45.64	35.75
B <sub>2</sub>	51.96	28.63	20.60	18.75	72.56	47.39
B <sub>3</sub>	68.60	41.60	27.61	32.95	96.21	74.56
F value of treatments	85.26***	34.63***	17.26***	6.53**	73.10***	22.77***
F value for the blocks	2.14	1.65	2.70	4.24	1.00	1.18
C.D. at the 5% level	2.026	1.668	1.675	3.685	2.928	5.001

\* Significant at the 5% level.

\*\* Significant at the 1% level.

\*\*\* Significant at the 0.1% level.

## Uptake of Phosphorus

### (a) Phosphate in the Dry Rice Tops (Table 3, column 4)

Since the supply of phosphate to the plants was limited and the yield of the rice tops increased with increasing amounts of nitrogen application, the percentage of phosphate in the tops decreased with increasing amounts of nitrogen application. Within the third-level treatments, the order of the percentage of phosphate in the rice tops was  $C_3=B_3=A_3 > S_3$ . At the second level it was  $C_2 > B_2=S_2 > A_2$ , and at the first level it was  $S_1 > B_1 > A_1 > C_1$ . Control plants had the highest percentage of phosphate in their tops.

### (b) Phosphate in the Water-logged Rice Tops (Table 4, column 4)

In this case, broadly speaking, the percentage of phosphate in the tops increased with increasing amounts of nitrogen application. With all the fertilizer treatments, plants receiving the first-level had the higher percentage of phosphate in their tops than did those given the second and third-level treatments. With ammonium bicarbonate and ammonium carbonate the same phosphate percentage was obtained at all the three levels of application. With the ammonium sulphate and ammonia treatments, the percentage of phosphate in the tops decreased at the second and the third-levels as compared with the first-levels. At the third-level, the order of percentage of phosphate in the rice tops was  $B_3=C_3 > A_3 > S_3$ , at the second-level it was  $B_2=C_2 > S_2=A_2$  and at the first-level it was  $B_1 > C_1=S_1 > A_1$ . Control plants had the lowest values.

In general, the water-logged rice tops had slightly higher percentage of phosphate than the dry-rice tops.

### (c) Total Phosphate Uptake of the Rice Tops:

At 5 per cent level of significance, the interpretation of the results is as follows:

#### (i) Dry Rice Tops (Table 8, column 2)

$B_3 \ C_3 \ C_2 \ B_2 \ S_3 \ A_3 \ S_2 \ C_1 \ S_1 \ B_1 \ A_1 \ \text{Control} \ A_2$

#### (ii) Water-logged Rice Tops (Table 8, column 3)

$C_3 \ B_3 \ S_3 \ C_2 \ B_2 \ S_2 \ B_1 \ A_3 \ C_1 \ A_2 \ S_1 \ A_1 \ \text{Control}$

### (d) Phosphate in the Dry Rice Roots (Table 5, column 5)

The percentage of phosphate in the dry-rice roots

decreased slightly with increasing amounts of nitrogen applied. Within the third-level treatments, values were in the order  $A_3 > S_3 > B_3 > C_3$ , at the second level it was  $A_2 > S_2 > B_2 > C_2$  and at the first level it was  $A_1=S_1 > B_1 > C_1$ . Ammonia treatments produced higher values at all the three levels of application.

### (e) Phosphate in the Water-logged Roots (Table 6, column 5)

Unlike the dry-rice roots, in this case, the percentage of phosphate in the roots increased with increasing amounts of nitrogen applied. Within the third-level treatments, values were in the order  $A_3=C_3 > B_3 > S_3$ . At the second level it was  $A_2 > B_2 > C_2 > S_2$  and at the first level it was  $A_1=S_1 > C_1=B_1$ . Ammonia caused the highest values at all three levels.

The percentage of phosphate in the dry-rice roots was significantly lower than in the corresponding water-logged roots.

### (f) Phosphate Uptake of the Rice Roots:

At 5 per cent level of significance the results yielded the following conclusions:

#### (i) Dry Rice Roots (Table 8, column 4)

$S_3 \ A_3 \ S_2 \ B_3 \ A_2 \ A_1 \ \text{Control} \ C_3 \ S_1 \ B_2 \ C_2 \ B_1 \ C_1$

#### (ii) Water-logged Rice Roots (Table 8, column 5)

$C_3 \ B_3 \ A_3 \ S_3 \ A_2 \ C_2 \ A_1 \ S_2 \ B_2 \ S_1 \ \text{Control} \ C_1 \ B_1$

### (g) Total Phosphate Uptake of the Rice Plants

At 5 per cent level of significance, the data yielding the following conclusions:

#### (i) Dry Rice Plants (Table 8, column 6)

$B_3 \ S_3 \ C_3 \ A_3 \ C_2 \ B_2 \ S_2 \ S_1 \ A_1 \ A_2 \ C_1 \ \text{Control} \ B_1$

#### (ii) Water-logged Rice Plants (Table 8, column 7)

$C_3 \ B_3 \ S_3 \ A_3 \ C_2 \ B_2 \ S_2 \ A_2 \ A_1 \ C_1 \ S_1 \ B_1 \ \text{Control}$

It is clear from the block totals that the water-logged rice plants took up significantly more phosphate than did the corresponding dry-rice plants.

TABLE 8—EFFECTS OF FERTILIZERS ON THE PHOSPHATE (P<sub>2</sub>O<sub>5</sub>) UPTAKE

(Figures expressed in mg.)

(Each figure represents an average of two blocks)

Treatments	Dry Rice Tops	Water-logged Rice Tops	Dry Rice Roots	Water-logged Rice Roots	Total Uptake of the Whole Dry Rice Plants	Total Uptake of the Whole Water-logged Plants
Control	27.15	18.18	19.33	39.72	46.48	57.90
C <sub>1</sub>	33.91	30.68	13.73	39.47	47.65	70.15
C <sub>2</sub>	44.18	44.64	17.79	52.15	61.98	96.79
C <sub>3</sub>	49.37	63.82	18.94	70.83	68.31	134.65
S <sub>1</sub>	33.52	24.88	18.41	44.28	51.93	69.16
S <sub>2</sub>	35.56	34.20	24.52	45.67	60.08	79.87
S <sub>3</sub>	40.86	45.76	31.96	60.01	72.83	105.77
A <sub>1</sub>	28.16	24.04	20.62	49.62	48.78	73.66
A <sub>2</sub>	25.74	25.57	22.41	52.27	48.15	77.85
A <sub>3</sub>	39.28	32.88	25.83	69.19	65.12	102.07
B <sub>1</sub>	29.52	33.23	16.42	32.94	45.94	66.17
B <sub>2</sub>	42.71	40.42	18.25	44.74	60.97	85.16
B <sub>3</sub>	53.99	57.12	23.67	70.30	77.67	127.43
F value for treatments	36.19***	64.00***	12.44***	3.76*	24.14***	9.43***
F value for the blocks	3.00	1.73	3.71	4.60	—	2.26
C.D. at the 5% level	1.838	2.103	1.692	8.101	2.761	9.718

\* Significant at the 5% level.

\*\* Significant at the 1% level.

\*\*\* Significant at the 0.1% level.

**Effect of Different Fertilizers on the Uptake of Potash of the Rice Tops***(a) Potash in the Dry Rice Tops (Table 3, column 5)*

The percentage of potash in the rice tops did not follow any consistent trend (due to the different fertilizer treatments). Within third-level treatments, the order of the percentage of potash in the tops was B<sub>3</sub> > C<sub>3</sub>=S<sub>3</sub>=A<sub>3</sub>. At the second level it was B<sub>2</sub> > S<sub>2</sub> > C<sub>2</sub> > A<sub>2</sub>, and at the first level it was S<sub>1</sub> > B<sub>1</sub> > A<sub>1</sub>=C<sub>1</sub>. Ammonia treatment resulted in lower percentage at all the three levels of nitrogen application than did the other treatments.

*(b) Potash in the Water-logged Rice Tops (Table 4, column 5)*

In general, the percentage of potash in the water-logged rice tops decreased with increasing amounts of

nitrogen applied. Within the third-level treatments, the order of percentage of potash in the tops was S<sub>3</sub> > A<sub>3</sub> > C<sub>3</sub> > B<sub>3</sub>. At the second level it was C<sub>2</sub> > S<sub>2</sub> > A<sub>2</sub> > B<sub>2</sub>, and at the first level it was S<sub>1</sub> > C<sub>1</sub> > A<sub>1</sub>=B<sub>1</sub>.

The variation in the percentage of potash between the dry and the water-logged rice tops was almost insignificant.

*(c) Potash Uptake of Rice Tops*

At 5 per cent level of significance the data yielded the following conclusion:

*(i) Dry Rice Tops (Table 9, column 2)*

B<sub>3</sub> C<sub>3</sub> B<sub>2</sub> S<sub>3</sub> C<sub>2</sub> S<sub>2</sub> A<sub>3</sub> B<sub>1</sub> C<sub>1</sub> S<sub>1</sub> A<sub>2</sub> A<sub>1</sub> Control

*(ii) Water-logged Rice Tops (Table 9, column 3)*

C<sub>3</sub> S<sub>3</sub> B<sub>3</sub> C<sub>2</sub> S<sub>2</sub> B<sub>2</sub> A<sub>3</sub> B<sub>1</sub> C<sub>1</sub> A<sub>2</sub> S<sub>1</sub> A<sub>1</sub> Control

TABLE 9—EFFECTS OF FERTILIZERS ON THE UPTAKE OF POTASSIUM BY PLANTS

(Figures expressed in mg.)

(Each figure represents an average of two blocks)

Treatments	Dry Rice Tops	Water-logged Rice Tops	Dry Rice Roots	Water-logged Rice Roots	Total Uptake of the Whole Dry Rice Plants	Total Uptake of the Whole Water-logged Plants
Control	82.43	65.47	60.56	62.61	143.00	128.08
C <sub>1</sub>	124.29	92.04	57.79	61.33	182.59	153.37
C <sub>2</sub>	154.65	142.84	68.22	68.41	222.88	211.26
C <sub>3</sub>	181.68	180.83	66.23	73.45	247.92	254.29
S <sub>1</sub>	108.94	76.71	59.48	76.22	168.43	152.93
S <sub>2</sub>	136.24	115.06	98.10	89.09	234.35	204.15
S <sub>3</sub>	168.63	166.59	129.98	117.19	298.61	283.78
A <sub>1</sub>	95.75	70.13	73.28	81.13	169.04	151.26
A <sub>2</sub>	99.98	83.70	83.21	87.40	183.20	171.10
A <sub>3</sub>	133.56	104.62	89.26	101.17	222.82	205.79
B <sub>1</sub>	126.83	93.05	56.93	53.47	183.77	146.53
B <sub>2</sub>	171.05	114.53	68.51	65.29	239.56	179.82
B <sub>3</sub>	212.72	159.00	92.28	92.80	305.00	251.81
F value for treatments	46.49***	60.25***	17.27***	3.32*	34.93***	12.24***
F value for the blocks	2.63	1.39	3.51	5.36	—	1.52
C.D. at the 5% level	6.999	6.219	6.360	12.425	10.601	17.369

\* Significant at the 5% level.

\*\* Significant at the 1% level.

\*\*\* Significant at the 0.1% level.

The block totals and the grand totals show that the dry rice tops took up significantly more potassium than did the water-logged tops. Also, under dry condition ammonium bicarbonate caused the highest uptake of K in the rice tops, whereas, under water-logged condition ammonium carbonate was the most effective in this respect.

(d) *Potash in the Dry Rice Roots* (Table 5, column 4)

Broadly speaking, (except in ammonium carbonate treatments), the percentage of potassium in the dry rice roots increased with increasing amounts of nitrogen application. Within the third level treatments, the order of the percentage of potash in the rice roots was  $S_3 > B_3 = A_3 > C_3$ . At the second level it was  $S_2 > A_2 > B_2 > C_2$  and at the first level it was  $A_1 > B_1 > C_1 > S_1$ . Ammonium carbonate-treated roots had the lowest values at all the three levels of nitrogen application.

(e) *Potash in the Water-logged Rice Roots* (Table 6, column 4)

Like the dry rice roots in this case (except in the ammonium carbonate treatments), the percentage of potassium in the roots increased slightly with increasing amounts of nitrogen applied. At the third-level, the order of the percentage of potassium in the rice roots was  $S_3 > A_3 > B_3 > C_3$ . At the second level it was  $A_2 > S_2 > B_2 > C_2$  and at the first level it was  $S_1 > A_1 > B_1 > C_1$ . At all the three levels of nitrogen ammonium carbonate treatments resulted in lower values than the corresponding ammonium bicarbonate, ammonium sulphate and ammonia treatments.

The water-logged rice roots had significantly lower values of potassium percentage than did the corresponding dry-rice roots.

(f) *Potash Uptake of Rice Roots*

At 5 per cent level of significance, the data yielded

the following conclusions:

(i) Dry Rice Roots (Table 9, column 4)

S<sub>3</sub> S<sub>2</sub> B<sub>3</sub> A<sub>3</sub> A<sub>2</sub> A<sub>1</sub> B<sub>2</sub> C<sub>2</sub> C<sub>3</sub> Control S<sub>1</sub> C<sub>1</sub> B<sub>1</sub>

(ii) Water-logged Rice Roots (Table 9, column 5)

S<sub>2</sub> A<sub>3</sub> B<sub>3</sub> S<sub>2</sub> A<sub>2</sub> A<sub>1</sub> S<sub>1</sub> C<sub>3</sub> C<sub>2</sub> B<sub>2</sub> Control C<sub>1</sub> B<sub>1</sub>

It is clear from the block totals that only insignificant difference in the potassium uptake of the rice roots between the dry and the water-logged conditions occurred.

(g) Total Potash Uptake of the Whole Rice Plants

At 5 per cent level, the interpretation of the results is as follows:

(i) Dry Rice Plants (Table 9, column 6)

B<sub>3</sub> S<sub>3</sub> C<sub>3</sub> B<sub>2</sub> S<sub>2</sub> C<sub>2</sub> A<sub>3</sub> B<sub>1</sub> A<sub>2</sub> C<sub>1</sub> A<sub>1</sub> S<sub>1</sub> Control

(ii) Water-logged Rice Plants (Table 9, column 7)

S<sub>3</sub> C<sub>3</sub> B<sub>3</sub> C<sub>2</sub> A<sub>3</sub> S<sub>2</sub> B<sub>3</sub> A<sub>2</sub> C<sub>1</sub> S<sub>1</sub> A<sub>1</sub> B<sub>1</sub> Control

The dry rice plants took up significantly more potassium than did the corresponding water-logged rice plants. Ammonium bicarbonate plants took up the highest amount of potassium under dry condition, whereas, under water-logged condition, ammonium carbonate-treated plants took up the highest amounts of potassium.

**Effect of Different Fertilizers on the Percentage of Carbon of the Rice Plants**

*Percentage of Carbon in the Dry and Water-logged Rice Tops (Tables 3 and 4, column 2)*

As it is quite clear from the results, the different fertilizer treatments did not affect the percentage of carbon of the rice tops. The water-logged rice tops, however, had slightly lower values than the corresponding dry rice tops.

*Percentage of Carbon in the Dry and Water-logged Rice Roots (Tables 5 and 6, column 2)*

Like the tops, in this case also, the various fertilizer

treatments did not produce any significant change in the carbon percentage values. The most interesting thing noticed in this experiment was the lower carbon percentage in the water-logged than in the corresponding dry rice roots. In general, the water-logged rice roots had 40 per cent lower values for carbon than the corresponding dry-rice roots. This was probably due to the anaerobic conditions prevailing under the water-logged conditions. As will be discussed later, there was hardly any evolution of carbon dioxide from the soil under water-logged conditions and hence, there was little direct absorption through the roots. This may explain the significance of carbon nutrition through the roots under the normal aerobic conditions.

**Effect of the Different Fertilizers on the Flowering and the Grain Yield of the Rice Plants**

According to the original plan, block 3 of both the dry and water-logged sets were retained until the plants reached maturity to study the effect of the different fertilizers on the reproductive development under dry as well as water-logged conditions.

The water-logged rice plants flowered three weeks earlier than the dry-rice plants (Fig. 3 & 4). In general, in both the sets, ammonium bicarbonate-treated plants flowered a little earlier than the corresponding ammonium carbonate, ammonium sulphate and Ammonia plants.

When the grains matured, the ears were harvested, dried and weighed.

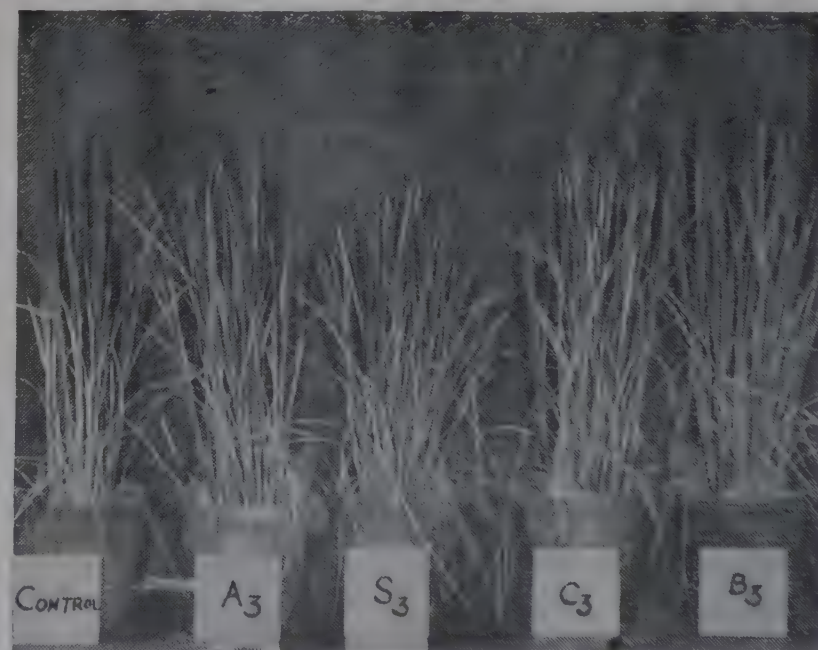


Fig. 3. Effect of Fertilizers on the Reproductive Growth (Dry Rice Plants).

Treatments: Control A<sub>3</sub> S<sub>3</sub> C<sub>3</sub> B<sub>3</sub>



Fig. 4. Effect of Fertilizers on the Reproductive Growth (Water-logged Rice Plants).

Treatments: Control A<sub>3</sub> S<sub>3</sub> C<sub>3</sub> B<sub>3</sub>

#### Yield of the Dry-rice Ears (Table 10)

Ammonium bicarbonate and carbonate-plants produced larger numbers of ears than did those receiving the other treatments. Within the third-level treatments, B<sub>3</sub> plants produced 14 ears as against 12, 10 and 7 produced by C<sub>3</sub>, S<sub>3</sub> and A<sub>3</sub> plants respectively. At the second level C<sub>2</sub> plants produced 11 ears as against 9, 7 and 6 produced by B<sub>2</sub>, S<sub>2</sub> and A<sub>2</sub> plants.

Finally, at the first-level, B<sub>1</sub> plants produced 10 ears as against 7, 6 and 6 produced by S<sub>1</sub>, C<sub>1</sub> and A<sub>1</sub> plants, control plants produced 6 ears.

TABLE 10—DRY MATTER YIELD OF RICE EARS PER POT (BLOCK 3)

Treatments	Yield of Dry Rice Ears		Yield of Water-logged Ears	
	Weight of Ears	Number of Ears	Weight of Ears	Number of Ears
Control	.316	6	.628	8
C <sub>1</sub>	.370	6	.789	8
C <sub>2</sub>	.688	11	1.092	13
C <sub>3</sub>	.901	12	1.948	19
S <sub>1</sub>	.360	7	.715	10
S <sub>2</sub>	.431	7	1.068	12
S <sub>3</sub>	.567	10	1.500	13
A <sub>1</sub>	.358	6	.365	6
A <sub>2</sub>	.369	6	1.184	9
A <sub>3</sub>	.522	7	1.439	12
B <sub>1</sub>	.476	10	.816	11
B <sub>2</sub>	.559	9	1.151	13
B <sub>3</sub>	.985	14	1.895	17

The yield of ears with the different fertilizer treatments was of the order—ammonium bicarbonate > ammonium carbonate > ammonium sulphate > ammonia. Control plants had the lowest yield of ears.

#### Yield of Water-logged Rice Ears (Table 10)

Under the water-logged conditions, C<sub>3</sub> plants produced 19 ears as compared with 17, 13 and 12 ears produced by B<sub>3</sub>, S<sub>3</sub> and A<sub>3</sub> plants respectively; C<sub>2</sub> plants produced 13 ears as against 13, 12 and 9 produced by B<sub>2</sub>, S<sub>2</sub> and A<sub>2</sub> plants, and B<sub>1</sub> plants 11 ears as against 10, 8 and 6 produced by S<sub>1</sub>, C<sub>1</sub> and A<sub>1</sub> plants. Control plants produced 3 ears.

### DISCUSSIONS

Unlike the upland (dry) soils, water-logged soils differ radically in the chemical regime of the different plant nutrients.

Under water-logged conditions, there is always a deficiency of oxygen due to the curtailment of gaseous exchange between soil and air. In order to survive under the anaerobic conditions, rice plants possess special adaptations. Rice plants are known to contain large air spaces in their roots,<sup>9</sup> and there is a continuity of these air spaces within the air channels in the shoot system.<sup>10</sup> Thus, rice roots are able to function more or less aerobically in an anaerobic environment.<sup>11, 12</sup> Unlike the upland soils, water-logged soils are characterised by a virtual absence of nitrate and accumulation of ammonia. Water-logging is known to increase the availability of phosphate to a considerable extent.<sup>12-17</sup> Submergence of a normal arable soil also brings an increase in the availability of silica.<sup>18, 19</sup> Japanese scientists<sup>20, 21</sup> found that the absorption of silica by rice plants results in the increased growth and yield of straw and grain and that it counteracts the harmful effects of excess of nitrogen. Water-logging also results in some release of iron and manganese ions. The pH value of a soil increases after water-logging, which has hardly any direct effect on the growth of rice plants, but the secondary effects of the pH may be considerable.

It is likely that the same variety of rice will behave differently with the same treatment under these two extreme conditions. Differences in the morphological appearances of the rice plants due to the different fertilizer treatments were more distinct under the water-logged than under the dry conditions. This was probably due to the "ammophile" nature of the rice plants.<sup>8</sup> Since there was hardly any evolution of carbon dioxide under the water-logged condition, the extra

supply of carbon in the ammonium carbonate and ammonium bicarbonate stimulated the vegetative growth of the rice plants as compared with the corresponding ammonium sulphate and ammonia-treated plants.

However, since the variety used was particularly suited for growing under dry conditions, the vegetative growth of the dry rice tops was better than those of the water-logged rice tops. Under dry conditions, B<sub>3</sub> proved superior to C<sub>3</sub> in the production of top yields. This was probably due to the extra carbon nutrition in the B<sub>3</sub>-treated plants as compared with the C<sub>3</sub>-treated plants. Under the water-logged conditions, however, C<sub>3</sub> proved to be superior to B<sub>3</sub> in this respect. This was probably due to the aerobic nature of CO<sub>2</sub> fixation by the roots.<sup>22-24</sup>

For the same amounts of nitrogen applied ammonium bicarbonate contains twice as much carbon as ammonium carbonate and under water-logged condition, because of the anaerobic environment, the rice roots probably failed to utilize some of the carbon supplied in the ammonium bicarbonate, whereas, the concentration of carbon in ammonium carbonate was such that the plants could deal with it under the prevailing conditions, since rice roots are known to function to a limited extent aerobically under anaerobic conditions due to the large air spaces present in their roots.

Water-logged plants produced significantly higher root yields than did the corresponding dry rice plants. Probably the special adaptation of the rice plants to thrive under anaerobic conditions, depends on a more extensive root system, which affords a better chance to function aerobically under the prevailing anaerobic conditions.

The percentage of nitrogen in both dry and water-logged rice tops were similar under identical treatment. Ammonia treatment resulted in the highest values under both conditions. This was probably due to the lower dry matter yields of ammonia-treated plants under both conditions.

Under the dry condition, ammonium bicarbonate treated plants probably fixed more carbon and hence showed higher uptake and utilization of nitrogen than did those receiving the other nitrogen treatments.<sup>25</sup> Under water-logged condition, however, ammonium carbonate was more effectively utilized; due to the "ammophile" nature of the rice plants maximum utilization of nitrogen occurred with the third-level treatments of the water-logged rice plants. Because the rice used was of an upland variety, the dry rice plants probably utilized more of nitrogen than did the corresponding water-logged rice plants. The water-

logged rice tops had significantly higher percentage and total uptake of phosphate than the dry-rice tops.

Dry-rice tops took up significantly more potassium than the water-logged rice tops although there was hardly any difference in the percentage of potassium between the two series. On the other hand, water-logged rice roots had significantly lower values for potassium than those of the corresponding dry-rice roots; there was hardly any difference in total potassium uptake between the dry and water-logged rice roots. However, the total potassium uptake of the whole dry-rice plants was significantly higher than that of the corresponding water-logged rice plants.

The maximum uptake of potassium under dry and water-logged conditions was by ammonium bicarbonate and ammonium carbonate treated plants respectively. The relatively higher uptakes of potassium by the ammonium bicarbonate and ammonium carbonate treated plants as compared to the ammonium sulphate and ammonia-treated ones was probably due to extra cation uptake consequent on carbon dioxide fixation by the roots.<sup>25</sup>

Carbon content in water-logged roots was 40 per cent lower than in the corresponding dry-rice roots. Anaerobic conditions resulting from the water-logging reduced greatly the mineralization of carbon from the soil. As a consequence, there was no carbon dioxide absorption through the water-logged rice roots, and hence the roots had to face a partial deficiency of carbon. This is confirmed by the lower values of the water-logged rice roots, and emphasises the significance of carbon nutrition through the roots under the normal aerobic conditions.

It has already been mentioned that the water-logged rice plants took up significantly more phosphate than did the dry rice plants. It is also known that water-logging results in an increase in the availability of silica and that absorption of silica by the rice plants results in an increase in growth and in yield of straw and grain and that it counteracts the harmful effects of excess nitrogen,<sup>20, 21</sup>. Probably for these reasons, among others, water-logged rice plants flowered three weeks earlier, produced higher yields of tops and roots and double the yield of ears as compared with the dry-rice plants. Ammonium bicarbonate treatment under dry condition and ammonium carbonate treatment under water-logged condition, however, produced the highest straw and grain yields probably due to carbon nutrition through the roots.

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# Agronomical Significance of Carbon Nutrition Part III—Studies on the Efficiency of Various Forms of Ammoniacal Nitrogen:

## RESPONSE OF AUS PADDY IN FIELD TRIALS\*

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The effects of four nitrogenous compounds, viz. ammonium carbonate, bicarbonate, sulphate and urea, on the growth and yield of *Aus* paddy have been studied in a field experiment and compared. The fertilizer nitrogen was applied in solution at a later stage of growth. The plants receiving ammonium carbonate and bicarbonate showed more rapid growth in terms of height, leaf area, tiller and higher grain and straw yields than those given the other nitrogenous compounds.

## Introduction

In the previous pot experiment† with *aus* paddy, it was observed that ammonium bicarbonate and carbonate are more effective for vegetative and reproductive

growth of rice plants than ammonium sulphate or ammonia. The present experiment was undertaken to confirm the above results under normal field conditions.

*Editor's Note:* This work together with the previous work by the author on this line appearing elsewhere (pp. 36-48) of this issue of TECHNOLOGY form the background of the work now under investigation in this laboratory. In a forthcoming issue of this bulletin, his results obtained here will be published.

\* This investigation was carried out by the author at Kalyani University, Kalyani, W. Bengal.

† pp. 36-48 in this issue

## Materials and Methods

(i) *Experimental Site & Cultivation*: The experiment was conducted at the Kalyani University agricultural farm. The area chosen for the trial has been under *aus* paddy for the previous two years, and the uniformity of crop ensured the uniformity of the site in respect of the nature and condition of the soil. Since differences in slope affect drainage, special care was taken to ensure that no part of the experimental site was worse-drained or more exposed than the remainder.

Since the shading effect of hedgerow plants often causes serious variations in plots situated too close to the headland, every effort was made to avoid this interference, and ultimately the piece of land selected was about 100 yds from the nearest hedge, which may be considered quite satisfactory in this respect. The soil type of the entire experimental area was sandy loam.

After the complete removal of the previous crop, the whole trial area was ploughed without a break, the headland being left outside the experimental area. For better tilth, the soil was then harrowed and laddered.

(ii) *Test Crop & Sowing*: *Dharia* variety of *aus* paddy was selected as the test crop because it responds very well to the higher levels of nitrogen application.

Since the experimental area was not too large, a hand-driven seed drill was used for sowing.

(iii) *Sources & Application of Ammoniacal Compounds*: Ammonium bicarbonate, -carbonate, ammonium sulphate and urea were selected as the nitrogenous sources and the levels of their applications were equivalent to 25, 50, 100 and 150 lbs of nitrogen per acre.

## Experimental

(a) *Design of Experiment*: Randomized block design with three replications.

(b) *Plot Dimensions & Row Widths*: A harvest plot size 1/100th of an acre has been found satisfactory in practice<sup>1</sup>. In fertilizer trials with rice, it is usual to discard two outside rows and 2 ft border from either end to avoid interference from the surrounding treatments. Since the row width chosen was 12" in., the total area of an individual plot including the discards was 44 ft × 15 ft which includes 15 rows of rice plants per plot. As it is quite apparent, the gross plot size was 0.015 acre, and the net plot size was 0.01 acre.

(c) *Method of Drilling and Plant Population*: Drilling was done across the line of the plough furrow on 8.6.63. Germination was almost complete by 11.6.63 and the plants were thinned on 28.6.63, every effort being made

to keep an uniform distance of 3 to 4 in. between the plants within the individual rows.

The number of seedlings within each plot retained after thinning was of the rate of  $130,500 \pm 50$  per acre, which can be considered as a fairly uniform population in different plots.

(d) *Preparation & Application of Fertilizers*: All the fertilizers were sampled and analysed for nitrogen before application, and on 7.8.63 applied in solution close to the root zone of the plants in the individual rows.

The total nitrogen applied was as follows:

Abbreviations	Fertilizers	Nitrogen, lbs/acre	Fertilizers, lbs/plot
Control	—	0	0
C <sub>1</sub>	Ammonium Carbonate	25	1.721
C <sub>2</sub>	"	50	3.443
C <sub>3</sub>	"	100	6.886
C <sub>4</sub>	"	150	10.329
B <sub>1</sub>	Ammonium Bicarbonate	25	2.367
B <sub>2</sub>	"	50	4.734
B <sub>3</sub>	"	100	9.468
B <sub>4</sub>	"	150	14.202
S <sub>1</sub>	Ammonium Sulphate	25	1.893
S <sub>2</sub>	"	50	3.787
S <sub>3</sub>	"	100	7.575
S <sub>4</sub>	"	150	11.362
U <sub>1</sub>	Urea	25	0.86
U <sub>2</sub>	"	50	1.721
U <sub>3</sub>	"	100	3.443
U <sub>4</sub>	"	150	5.164

(e) *Effects of Fertilizers on the Growth of Paddy*: In order to magnify the effect of carbon nutrition through roots from ammonium carbonate, bicarbonate and urea, fertilizers were applied at the peak period of the vegetative growth of the plants. Two days after the application of the fertilizers viz. ammonium bicarbonate and carbonate, treated plants showed signs of scorching of the leaves. Within the fourth level treatments, the symptoms were more severe than with the third, second and first. The plants, however, started to recover within a week and they almost completely recovered within a fortnight. Ammonium sulphate and urea treated plants did not show any scorching.

A month after the application of the fertilizers, the effects of the various forms of nitrogen on the vegetative and reproductive growth of the rice plants became very prominent. The efficiencies of the different fertilizers on the acceleration of the vegetative and reproductive

growth as indicated by the heights, leaf areas, colour of the leaves and time of earing was of the order of ammonium bicarbonate > ammonium carbonate > urea > ammonium sulphate > control.

(f) *Harvesting*: When the grain matured, the plants were harvested on 15.9.63. The straw and the grains were then weighed immediately and samples were taken for the determination of moisture contents.

## RESULTS

### Effect of the Different Fertilizers on the Dry Matter Yield of Rice Straw

*Dry Matter Yield of Rice Straw* (Table 1, Column 1): Statistical examination of the results confirmed that correlation between the dry matter yield of the rice straw and the different fertilizer treatments, significant at 0.1 per cent level can be established. At 5 per cent level, the statistical interpretation of the results is as follows:

C<sub>4</sub> B<sub>4</sub> U<sub>4</sub> S<sub>4</sub> C<sub>3</sub> B<sub>3</sub> S<sub>3</sub> U<sub>3</sub> C<sub>2</sub> B<sub>2</sub> U<sub>2</sub> S<sub>2</sub> C<sub>1</sub> B<sub>1</sub> U<sub>1</sub> S<sub>1</sub> Control.

*Dry Matter Yield of Rice Grains* (Table 1, Column 2): The observed differences in the dry matter yield due to the treatments are significant at the 0.1 per cent level. At 5 per cent level, the conclusion is as follows:

B<sub>4</sub> C<sub>4</sub> U<sub>4</sub> S<sub>4</sub> C<sub>3</sub> B<sub>3</sub> U<sub>3</sub> S<sub>3</sub> B<sub>2</sub> C<sub>2</sub> U<sub>2</sub> S<sub>2</sub> B<sub>1</sub> C<sub>1</sub> U<sub>1</sub> S<sub>1</sub> Control.

## DISCUSSIONS

The effect of ammonium bicarbonate and carbonate on the vegetative and reproductive growth of rice plants seems to afford considerable promise of commercial use. The ammonium bicarbonate and -carbonate-treated plants showed better rates of growth, larger leaf areas, thicker stems and larger straw and grain yields than the corresponding urea and ammonium sulphate treated plants, Bhan<sup>2</sup> et al found that when carbon dioxide is fixed by roots, more cations are taken up. They also noted that NH<sub>4</sub> ion is taken up vigorously as a result of carbon dioxide fixation by roots. Jackson and Coleman<sup>3</sup> showed that the above fixation in the presence of NH<sub>4</sub> ions results in the formation of more amino acids rather than non-amino organic acids. In the case of rice plants, also, probably the same type of fixation of carbon dioxide and ammonia occurred. When ammonium bicarbonates and carbonates were supplied to the plants, carbon dioxide was probably fixed vigorously for the first few days and during that time due to the

abundance of readily available ammonia, it was taken up vigorously. Although urea gets hydrolysed into ammonium carbonate, the beneficial effect of carbon nutrition was not observed probably because of the fact that when urea is top dressed, the urea molecule itself is utilized by the rice plants which in due course proves toxic<sup>4</sup>. In the case of ammonium sulphate treatments, this extra uptake of ammonia due to carbon dioxide fixation did not occur. So ultimately the ammonium bicarbonate and carbonate-treated plants had a better start than the corresponding ammonium sulphate treated ones. They had an extra reserve of carbon and nitrogen, and hence produced a vigorous vegetative growth resulting in a rapid higher uptake of all the other nutrients, as compared with the other treatments. They maintained their superiority all through because of the vigorous start they attained due to carbon dioxide fixation and the consequent extra uptake of ammonium nitrogen. As a result of the vigorous vegetative growth, the ultimate dry matter yields of ammonium bicarbonate and carbonate treated plants were higher than the corresponding two other fertilizer treatments.

TABLE 1—DRY MATTER YIELD OF RICE STRAW & GRAINS, LBS/PLOT

(Each figure represents an average of three replicates.)

Treatments	Column I Straw	Column II Grains
Control	74.3	17.3
C <sub>1</sub>	117.0	23.0
C <sub>2</sub>	169.3	28.0
C <sub>3</sub>	188.0	34.3
C <sub>4</sub>	197.3	37.3
B <sub>1</sub>	114.7	23.0
B <sub>2</sub>	166.7	28.3
B <sub>3</sub>	185.7	32.0
B <sub>4</sub>	197.0	37.7
S <sub>1</sub>	110.3	19.0
S <sub>2</sub>	152.3	24.5
S <sub>3</sub>	182.7	31.2
S <sub>4</sub>	191.3	35.7
U <sub>1</sub>	112.7	21.8
U <sub>2</sub>	158.3	27.5
U <sub>3</sub>	181.7	31.8
U <sub>4</sub>	192.0	36.0
'F' Value	1686***	137.4***
Standard Error of treatment mean	0.929	0.552
Critical difference at the 5% level	2.67	1.58

\*\*\* Significant at 0.1% level.

## Utilisation of Ammonium Carbonate & Bicarbonate in the Tropical Agriculture

Tropical soils are known to contain considerably less (in general about 10 times less) organic matter as compared with those of the temperate soils. High temperature and rainfall in the tropics encourage vigorous bacterial growth and activity and as a consequence, the decomposition of organic matter is extremely rapid.

Because of the low organic matter content of the tropical soils, the soil respiration carbon dioxide given out due to the bacterial activity in the soils is very low and as such, there is every possibility that carbon supply to the plants becomes a limiting factor for their optimum growth and development. Such disastrous results, like plants becoming tall, thin and extremely susceptible to drought and diseases, obtained in tropical agriculture after heavy applications of nitrogen may be due to the proportionately less carbon nutrition of the plants from the soils.

It is known to every tropical agriculturist that, in general, for the same amount of nutrient application, better crop responses can be obtained from organic and green manures than those from the mineral fertilizers. It has been found that the carbon dioxide concentration of the soil can be increased 2 to 3 fold by the use of manures on the surface of the soil<sup>5</sup>. Yurbitsky<sup>6</sup> concluded that the favourable influence of manure on the cultivation of cucumber and sugarbeet was partly due to increased uptake of carbon dioxide by the plants e.g. uptake by roots as well as by the aerial organs. Reinau<sup>7</sup> presented a hypothesis that the carbon dioxide originating in the soil during the decay of organic matter is an important factor causing heavy yields of close standing crops. Kuzin and Merenova<sup>8</sup> confirmed the hypothesis of Tiulin<sup>5</sup>, Yurbitsky and Reinau<sup>7</sup> regarding the uptake of carbon from the organic manures through the plant roots. In their experiments they used wheat plants and supplied them with organic manures containing  $^{14}\text{C}$ . They noted that 180 days old wheat plants absorbed carbon dioxide readily from the manure, particularly in the early stages when the concentration of carbon dioxide in the soil was high.

Merenova and Kuzin<sup>9</sup> investigated the uptake of carbon from green manures under field conditions. They noted that the seedlings grown in the soil containing green manure marked with radioactive carbon, quickly and directly took up  $^{14}\text{C}$  from the water-soluble fraction of the manure. Labelled carbon was also absorbed indirectly in the form of carbon dioxide produced by the microbial decomposition of the insoluble fraction of the manure.

D'yakonova<sup>10</sup> believes that organic manures supplemented to a great extent the carbon assimilated by the plants. In her experiments she found that cropped soil supplied more than 50 per cent of the total carbon dioxide assimilated by the standing crop.

So it now can be concluded that one of the main reasons of the better response of crop plants to organic manures than to mineral fertilizers is the increased carbon nutrition through the roots as well as through the leaves, which is not often realised.

It is well-known that both carbohydrate and nitrogenous compounds are assimilated in relatively large quantities especially during cell division and enlargement phases of growth. If the supply of nitrogenous foods to any actively growing vegetative meristem is abundant relative to the supply of carbohydrate food, a large quantity of protoplasm will be formed relative to the amount of cell-wall material constructed. The resulting cells will ultimately be large, thin-walled, and will contain an abundance of protoplasm. Ultimately, the tissues composed mostly or entirely of such large, thin-walled cells are usually soft and succulent. The proportion of mechanical tissue developing under such metabolic conditions is ordinarily small. So, as a result of relatively large proportion of nitrogen to carbohydrate foods within a plant, morphological imbalance becomes evident<sup>11</sup>. As it is well-known, plants exhibiting this type of vegetative development are comparatively unfruitful and are very much susceptible to drought. High levels of nitrogen application in tropical soils normally result in crops having the above physiological and morphological features.

Under the reverse metabolic conditions, i.e. when carbohydrate foods are relatively more abundant than the nitrogenous ones, proportionately more cell-wall structures and less protoplasm will be fabricated. The resulting cells will be small and thick-walled, and will contain comparatively little protoplasm. The tissues composed largely or entirely of such cells are usually compact and more or less woody. The development of the fibres and mechanical tissues generally is also favoured by an excess of carbohydrate relative to nitrogenous foods. Plants exhibiting this type of vegetative development are comparatively more fruitful and are considerably more drought-resistant; and hence they are more desirable in tropical agriculture. So proportionately more carbon nutrition much more than nitrogen is of supreme importance in the tropical agriculture than nitrogen nutrition; mineral nitrogenous fertilizers should therefore always be supplemented with carbonaceous fertilizers. This carbon can be supplied in

the form of organic or green manures; but these are bulky and involve greater expense for transport and application. Furthermore, in order to avoid immobilisation of nitrogen immediately after the application of the organic manures to the soils, they must be applied in advance of the actual sowing. Unfortunately under tropical conditions, before the crop is sown, almost all the carbon of the organic manures is lost due to quick decomposition. Carbon fertilization, to be effective, should be done at the peak period of the vegetative growth of the crops. Organic manures cannot be used for top-dressing of the crops like ammonium carbonate or -bicarbonate, which provides nitrogen as well as carbon, and thus balances the vegetative growth of the growing crops.

At present, the two most popular ammoniacal nitrogenous sources are ammonia and ammonium sulphate. In U.S.A. ammonia is extensively used in irrigation which is highly mechanised. In the tropics, because of the expensive irrigation plants and higher transport costs ammonia is not commonly used, ammonium sulphate is the most popular source of nitrogen. Ammonium sulphate is known to be an acid-producing fertilizer, and its continuous use in the tropical soil, which is more poorly buffered than the temperate soil, without any measure to neutralise the acidity produced, lowers the pH considerably, which is detrimental to the crops.

The commercial manufacture of ammonium sulphate involves the preparation of the ammonium carbonate before it reacts with gypsum. Gypsum is comparatively costly and its transport involves an extra cost. It would, therefore, be logical to conclude that the cost of ammonium carbonate is cheaper per unit of nitrogen than ammonium sulphate.

## Conclusion

Ammonium carbonate and -bicarbonate are more efficient for vegetative as well as reproductive growth of the plants than ammonium sulphate, the commonest ammoniacal fertilizer used at present.

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# Dry Box Purification for Removal of Hydrogen Sulphide from Carbon Dioxide

By

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Experiments were carried out to evaluate the activity of precipitated iron oxide for removal of hydrogen sulphide in presence of high concentration of carbon dioxide at linear gas velocities 6, 7 and 8 mm/sec. and bed heights 6, 12, 18 and 24 inches. Maintaining 600 ppm. hydrogen sulphide in the inlet gas and feeding the theoretical quantity of air in the system for regeneration, it was found that at linear velocity 8 mm./sec. while the bed heights were 6, 12, 18 and 24 inches, the corresponding hydrogen sulphide concentrations in the outlet gas were 203, 38, 7 and zero ppm. respectively. Similarly, at a linear velocity 6 mm./sec., hydrogen sulphide concentration became zero when the bed height was 12 inches and above. With the 3 tubes filled up to 18 inches with oxide, hydrogen sulphide concentration of 3-4 ppm. could be obtained in the outlet gas after 467 working days. With the first tube refilled with fresh oxide and placed at the end, it took another 266 days to obtain 2-3 ppm. of hydrogen sulphide at the exit of the series.

The removal of hydrogen sulphide from fuel and synthesis gases by dry box purification is one of the oldest techniques in gas industry. The process was developed as early as 1859 and was first introduced in the U.K., followed by the continental countries and the U.S.A.

The basic principle of dry box purification is the oxidation of hydrogen sulphide to sulphur in presence of a carrier. The rate of oxidation is very slow at ordinary temperature in the absence of any oxygen-carrier, and the hydrated iron oxide is known to be the best carrier. The hydrated forms of iron oxide may be present as: (i)  $\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; (ii)  $\gamma$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; (iii)  $\delta$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , all crystalline varieties, and (iv) the amorphous variety. All these forms react with hydrogen sulphide,<sup>1</sup> but  $\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\gamma$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  are very useful for the removal of the latter. The significance of iron oxide as a carrier for  $\text{H}_2\text{S}$  removal lies in the fact that it not only reacts with hydrogen sulphide according to:  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ , but the sulphided iron can be revived in presence of oxygen as:  $\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{S}$ . So the overall reaction comes to:  $\text{H}_2\text{S} + \text{O} = \text{H}_2\text{O} + \text{S}$ . The activity of iron oxide persists for a number of cycles and generally it can be used till sulphur content rises to 50 per cent of the dry oxide.

Apart from the crystalline form, the size, porosity, moisture content and pH of the iron oxide grains are

important factors, which influence the absorption of hydrogen sulphide by iron oxide. The other factors influencing the rate of reaction are space velocity of the gas and temperature of the oxide bed, etc. In the industrial unit the optimum temperature is known to be in the range of 30°-40°C, and pH of the oxide is controlled between 8.0-10.0. If the pH of the oxide grain drops and the oxide slowly gets dehydrated, a mixture of  $\text{FeS}_2$  and  $\text{Fe}_8\text{S}_9$  are formed in the system which is undesirable because these two sulphides are gradually converted to sulphate and are therefore lost from the system as active constituents.

Bog ore, Luxmasse and precipitated iron oxide are generally used as the purifying mass. The precipitated iron oxide may be present either as  $\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\gamma$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  depending on the method of preparation, but in the case of bog ore and Luxmasse iron is present as  $\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . In the iron oxide process of purification, iron content of the dry oxide need not be very high, because sulphur formed after oxidation does not remain on the surface but migrates to the core of the oxides grain. This phenomenon was studied by Avery,<sup>2</sup> and subsequently by Dent and Moignard<sup>3</sup>. The exact mechanism of this migration process is not fully clear, but according to the authors probably water and carbon dioxide should be present in the system to facilitate the migration. Griffith and Morcom<sup>1</sup> have observed that any ferric oxide or its hydrate will react with hydrogen

sulphide, but after revivification these will reappear in the system as  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ .

The reaction between iron oxide and hydrogen sulphide and its revivification are both exothermic, but in the latter case liberation of heat is considerable. Due to this heat release, moisture from the oxide gradually evaporates away. In extreme cases, the iron oxide in the first box may even dry up when it is very active and hydrogen sulphide concentration in the inlet stream is very high, resulting in the caking and deactivation of the mass. Generally, 80 per cent removal of hydrogen sulphide in the first box is quite satisfactory.

There are many references in the literature for the removal of hydrogen sulphide from coke oven, town and synthesis gases by dry box purification method, but those relating to its use for removal of hydrogen sulphide from carbon dioxide are scarce. Carbon dioxide is generally cleansed of hydrogen sulphide by active carbon and inorganic salts like those of zinc and cadmium. The present investigation is related to hydrogen sulphide absorption capacity of iron oxide in presence of high concentration of carbon dioxide, and in all the experiments the precipitated iron oxide developed in this Division<sup>4</sup> of the FCI Ltd. has been used.

## Results & Discussions

An all-glass apparatus consisting of 3 purifying tubes of 39 mm. dia. and 650 mm. length and provided with suitable cross-over device for connecting them either in series or in parallel was fabricated. All the tubes were filled with the purifying mass of the following composition: Iron oxide 40, Wood shaving 35, and Moisture 25 per cent; Bulk density—0.528 g./cc.

*Effect of Change in Linear Velocity & Height of Purifying Mass:* The effect of change in linear velocity and height of the purifying material was studied (Table 1.)

Carbon dioxide from the degasification system of ammonia plant of Sindri Fertilizers Factory was chosen

as a carrier for hydrogen sulphide in the present investigation. Its purity was about 85 per cent and its hydrogen sulphide content varied between 200-500 ppm. Because of the fluctuation of concentration over a wide range, hydrogen sulphide from the carbon dioxide stream was scrubbed out with cadmium chloride solution. The feed gas was saturated with water vapour so that moisture content of the oxide did not vary to a great extent. In each experiment, predetermined quantities of hydrogen sulphide and air were dosed in the sulphur-free carrier gas.

It has been found that at the maximum linear velocity of 8 min./sec., when the height of oxide bed is 6" and only one tube is in line, hydrogen sulphide in the tubs outlet is 202 ppm. (Table 1). When the 3 tubes are in series (the cumulative height of oxide 18") under the same condition, hydrogen sulphide concentration is 9 ppm. in the outlet gas. With 6 mm./sec. linear velocity and total oxide height of 12", hydrogen sulphide concentration in the outlet gas is nil whether the oxide is packed in one tube or in two tubes each of 6" height. Where the total height of the oxide bed is 24", whether it is packed in one tube or in three, the amount of hydrogen sulphide is always nil in the outlet gas.

*Capacity of Purifying Material:* Next, to evaluate the capacity of the oxide, and determine the limiting conditions for changing it, experiments were carried out as below:

Three tubes connected in series were filled up with the oxide mass up to a height of 18" when the volume of the oxide in each tube was 545 c.c. of BD 0.528 g./c.c. The composition of the oxide mass was the same as indicated earlier.

Carbon dioxide gas of about 85 per cent purity was scrubbed as usual for the removal of hydrogen sulphide before it was fed into the purifying tubes. A gas velocity of 7 mm./sec. was maintained throughout. Measured amounts of hydrogen sulphide were introduced into the gas stream at a controlled rate, and a theoretical amount

TABLE 1— $\text{H}_2\text{S}$  AT EXIT OF EACH BOX FOR DIFFERENT HEIGHTS OF MASSES, PPM

Linear Velocity of Gas Thro' Oxide Mass, mm./sec.	6" Ht			12" Ht			18" Ht			24" Ht		
	I Tube	II Tube	III Tube	I Tube	II Tube	III Tube	I Tube	II Tube	III Tube	I Tube	II Tube	III Tube
6	187	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
7	195	23	traces	22	Nil	Nil	traces	Nil	Nil	Nil	Nil	Nil
8	203	40	9	38	Nil	Nil	7	Nil	Nil	Nil	Nil	Nil

of air was injected.

Initially, carbon dioxide gas containing about 600 ppm. of hydrogen sulphide was passed through the oxide, but even after several days no sulphide could be detected at the exit of the third tube. If hydrogen sulphide in the feed stream was maintained at 600 ppm., the period of fouling up to the stage when exit gas would contain hydrogen sulphide of the order of 3-4 ppm. was expected to be very long. Therefore, to shorten the duration of the experiment at the initial stage, the oxide was fouled at an accelerated rate by dosing higher concentration of hydrogen sulphide in the feed stream, and its concentration was varied between 0.2 to 5.0 per cent. This rate was continued till a substantial amount of the oxide in the tubes was sulphided which could be followed by observing the movement of the distinct boundary of the black sulphided zone. When about 75 per cent of the oxide was fouled, hydrogen sulphide in the feed was brought down to the controlled rate of 600 ppm., and the experiment was continued till about 3-4 ppm. of hydrogen sulphide was obtained at the exit of the third tube (Table 2A). With 3-4 ppm. of hydrogen sulphide at the exit of tube III it was found that a total of 202 l. of pure hydrogen sulphide has streamed through the oxide mass. This volume of pure hydrogen sulphide is converted to an equivalent volume of feed gas containing 600 ppm. of hydrogen sulphide, which works out at about 336 m<sup>3</sup> of gas at room temperature and pressure; and this corresponds to working of 467 days with a gas stream having 600 ppm. of hydrogen sulphide.

TABLE 2A—TUBES I, II & III IN SERIES

Sl. No.	Total Vol. of H <sub>2</sub> S Passed Thro' Tube I.	Total Vol. of Gas Passed Thro' Tube (600 ppm H <sub>2</sub> S), m <sup>3</sup>	Total Period of Fouling, days	H <sub>2</sub> S at Exit, ppm.
1.	0.432	0.72	1	Nil
2.	0.864	1.44	2	Nil
3.	1.296	2.16	3	Nil
450	194.4	324	450	Nil
465	200.9	334.8	465	3
466	201.3	335.5	466	4
467	201.7	336.2	467	4

TABLE 2B—TUBES II, III & I IN SERIES

Sl. No.	Total Vol. of H <sub>2</sub> S Passed Thro' Tube I.	Total Vol. of Gas Passed Thro' Tube (600 ppm H <sub>2</sub> S), m <sup>3</sup>	Total Period of Fouling, days	H <sub>2</sub> S at Exit, ppm.
1.	0.432	0.72	1	Nil
2.	0.864	1.44	2	Nil
3.	1.296	2.16	3	Nil
260	112.3	187.2	260	Nil
264	114.0	190.1	264	2
265	114.4	190.8	265	4
266	114.9	191.5	266	5

When hydrogen sulphide content at the exit of tube III was 3-4 ppm., tube I was discharged and filled with fresh oxide; and all the three tubes were again put in series placing tube II in the first position and tube I at the end. In this case also, accelerated fouling method was adopted initially. At the latter part, the experiments were continued with hydrogen sulphide concentration of 600 ppm. in the feed gas (Table 2B). With about 3-4 ppm. of hydrogen sulphide at the exit of the tube I, it was found that a total volume of 115 l. of hydrogen sulphide has passed through the series. In this case, however, on the same basis as explained earlier, the total period of fouling at this stage works as 266 equivalent days.

#### Acknowledgement

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# Corrosion Cracking of Mild Steel in an Ammoniacal Medium: A Case History

By -

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Extensive corrosion cracking has been observed in the mild steel equipment which comes in contact with regenerated liquor in the carbon dioxide scrubbing section in the Rourkela fertilizer plant. The regenerated liquor contains dissolved ammonia, hydrogen sulphide and cyanide. The cracking has been found to be intergranular, and the failure of the equipment is ascribed to stress corrosion.

## Introduction

Mild steel equipment are used extensively for handling ammoniacal solutions, and are generally considered resistant to such media, although corrosion may take place under special circumstances<sup>1</sup>. Recently, failure of some mild steel equipment had occurred in an ammoniacal medium in the fertilizer factory at Rourkela. In the carbon dioxide scrubbing section of the ammonia plant in this factory, the majority of equipment is made of mild steel. Carbon dioxide from coke-oven gas is absorbed by aqua ammonia, and the spent liquor is regenerated by heating it to a temperature of 87°-89°C by indirect steam. The regenerated liquor is cooled\* in two stages viz. (1) by exchanging heat with spent liquor in a series of aluminium heat exchangers and (2) by cooling with process water in a series of mild steel shell and tube coolers, where the liquor is on the shell-side and water on the tube side. Cracks have been found to develop on the mild steel shells and headers near the welds and also on the outside surface of some tubes, which were in contact with the regenerated liquor. The temperature of the liquor was 60°-65°C at the inlet and 35°-40°C at the outlet.

Weight-loss experiments and metallographic examinations were carried out to find out the causes of corrosion cracking of the mild steel equipment. The results are reported in this paper.

## Experimental

**Weight Loss Experiments:** Weight loss experiments were carried out in a sample of regenerated liquor

\* The flow diagram of the regenerated liquor cooling system is shown in Fig. 1 on page 24 in this issue.

collected from Rourkela plant as well as in the liquor from Sindri Plant. The analyses of these liquors are given in Table 1. Rectangular test pieces were cut out from the undamaged portions of the mild steel shells and headers in the Rourkela plant. The samples\* con-

TABLE 1—ANALYSIS OF REGENERATED LIQUORS

Ingredients	Rourkela Liquor, g./l.	Sindri Liquor, g./l.
Total NH <sub>3</sub>	30-35	28-35
Combined CO <sub>2</sub>	18-21	30-40
H <sub>2</sub> S	0.15-.22	Trace
HCN	.002-.006	—
Cl	810	Trace
SO <sub>4</sub>	100	Trace
pH	10.5	10.5

formed to the German specifications 35.29 DIN and 37.21 DIN. For comparison, a sample of mild steel manufactured by Messrs Tata Iron & Steel Company and conforming to specification IRS-M-16/49 was also used in these experiments. The surfaces of the test coupons were prepared by emery paper; they were then degreased in boiling toluene, washed with alcohol, dried and weighed. The coupons were kept completely immersed in liquors contained in polythene bottles, and were hung by glass hooks inserted through holes in rubber stoppers closing the mouths of the bottles. The polythene containers were kept in a thermostatic bath for 24 hr at 60°±0.1°C. After the experiments,

\* The detailed description of the samples of the failed portion is given in Table 1 on page 26 in this issue; the photographs of the 'as received' failed specimens are given in Figs. 2A, 2B & 2C on page 25.

the coupons were taken out, treated with inhibited sulphuric acid and the cleaning and drying process was repeated. They were then weighed.

*Metallographic Examinations:* Samples were cut out from the cracked and uncracked portions of the mild steel tube, shell and header. They were polished, etched and examined under the metallographic microscope (Figs. 1 & 2).

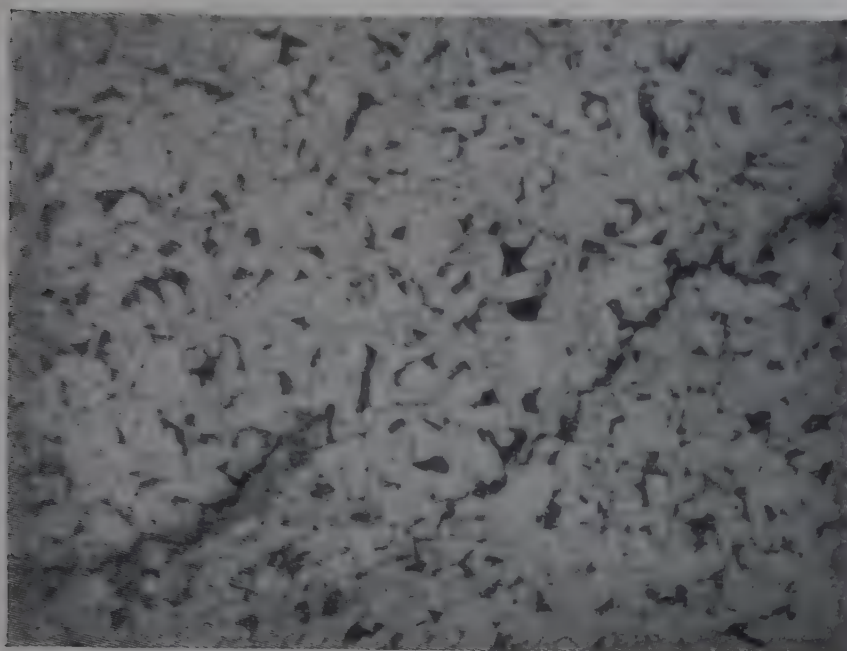


Fig. 1 Photomicrograph showing Typical Branched Intergranular Cracking of Mild Steel Header. ( $\times 70$ ). Nital Etch

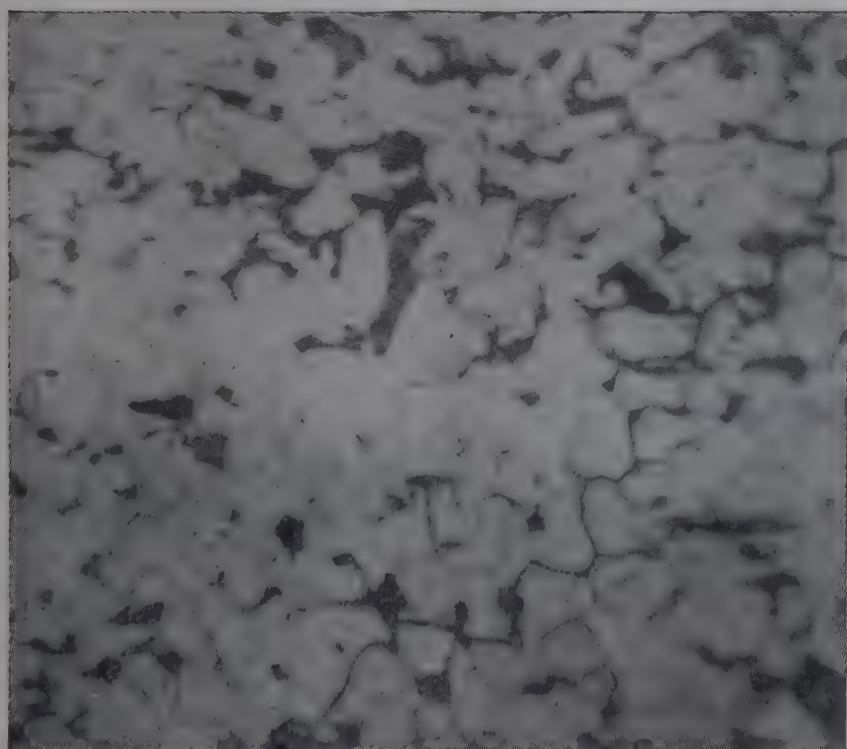


Fig. 2. Photomicrograph showing Branched Intergranular Cracking of Mild Steel Tube. ( $\times 450$ ). Nital Etch

## RESULTS & DISCUSSIONS

Since chlorides and sulphates are known to aggravate corrosion, intentional additions of these were made in the Sindri liquor so that their concentrations were the same as in the case of Rourkela liquor. The results show that there is considerable corrosion of mild steel in regenerated liquor at Rourkela plant (Table 2); the corrosion rate is, however, negligibly small in the case of Sindri liquor, although its contents of chloride and sulphate were brought to the same level as in the Rourkela liquor. These results indicate that the presence of hydrogen sulphide in substantial amount in the Rourkela liquor may be the reason for its corrosive nature. The Sindri liquor contains only a trace of hydrogen sulphide, and that may be the reason of its practically non-corrosive behaviour to mild steel. After keeping for some time, the hydrogen sulphide content in the Rourkela liquor was reduced to nil; the concentrations of other important constituents did not, however, change appreciably. The corrosion rate was, however, reduced to nil. The presence of cyanide in the Rourkela liquor in addition to hydrogen sulphide is expected to aggravate the corrosion by the latter. The primary product of hydrogen sulphide corrosion would be

TABLE 2—CORROSION OF MILD STEEL IN REGENERATED LIQUOR

Vol. of solution	..	..	275 ml.
Area of the test coupon	..	..	25-28 sq. cm.
Temp.	..	..	$60^{\circ} \pm 0.1^{\circ}\text{C}$
Duration of Test	..	..	24 hr.

The results are expressed as mg/sq dm/day

Media	Tata M.S.	Rourkela M.S.	Remarks
1. Rourkela Regenerated Liquor	31.5	105.6	In both cases a very dark tenacious adherent deposit is formed on the surface of the specimen. In addition some loose deposits are seen clinging to the surface while a large quantity of deposit settles at the bottom of the test vessel.
2. Rourkela Regenerated liquor containing no $\text{H}_2\text{S}$	No corrosion	No corrosion	Specimen is bright and shining.
3. Sindri Regenerated liquor+800 ppm $\text{Cl}_2$ +100 ppm $\text{SO}_4$	—	1.4	Specimen is bright and shining.

ferrous sulphide, and this would be converted by cyanide first to ferrous cyanide, then to ferrocyanide and finally to ferric ferrocyanide.

Metallographic examinations of the cracked and uncracked portions of the mild steel tubes, shells and headers from the Rourkela plant show that they have the normal ferrite-pearlite structure characteristic of annealed low-carbon steel. The cracked specimens show intergranular cracking pattern (Figs. 1 & 2). The cracking pattern is typical of stress-corrosion failure of mild steel that occurs in solutions of nitrates<sup>2</sup> and hydroxides<sup>3, 4</sup>

The intergranular cracking occurred mostly near the welded seams. The stress-corrosion cracking was most probably caused by the conjoint action of the residual stress left after welding and the corrosive regenerated liquor containing hydrogen sulphide, cyanide and ammonia.

A stress-relief anneal of welded portions at 600°-650°C may, therefore, be a remedy of the trouble attending stress-corrosion cracking of mild steel equipment in the regenerated liquor containing hydrogen sulphide, cyanide and ammonia. Furnace annealing is not, however, possible for complicated equipment. For such cases, a controlled low temperature stress-relieving

process<sup>5</sup> has been developed. In this process two oxy-acetylene torches are allowed to move in tandem along two strips one on each side of a welded joint so that they are heated to about 260°C.

The replacement of mild steel coolers with those made of aluminium would also be a remedy of the trouble, since no corrosion was observed in Rourkela plant with aluminium coolers which were in contact with the regenerated liquor.

#### Acknowledgements

The authors wish to thank Dr. K. R. Chakravorty, General Manager, for his interest in this work. Thanks are also due to Dr. A. D. Pandey and to Messrs M. P. Gupta and H. N. Ghosh for assistance.

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## A Rapid Method of Determination of Permanganate Value of Water and Effluents

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A method of determining permanganate value of effluents from various chemical plants and of raw water has been standardized. It is time-saving, and takes only about 15 minutes instead of about 3 to 4 hr as in the established permanganate value test.

As early as in the latter part of the 19th century, the necessity of evaluation of the pollutional characteristics of waters was considered and the Royal Commission on Sewage Disposal in U.K. laid down standard test procedure for assessment of pollution based

on the determination of dissolved oxygen depletion in water under standard conditions. The test is widely known as biochemical oxygen demand or simply B.O.D Test<sup>1</sup> (Lederer).

The temperature of 65°F (18.3°C) was adopted for

the B.O.D. test because it was unusual for the British streams to exceed this value even during the summer months. The Ministry of Housing and Local Government<sup>2</sup> (1956) have later recommended that the incubation temperature for the B.O.D. should be 20°C to bring the test in line with the American and continental practices. The term B.O.D. at present, unless otherwise stated, stands for biochemical oxygen demand in 5 days at 20°C. The B.O.D. of a sample is the quantity of dissolved oxygen in mg. required during stabilization of the decomposable organic matter by aerobic biochemical action in one litre of water.<sup>3</sup>

The principal disadvantage of the B.O.D. test is that it takes five days to complete and that it is also dependent upon a number of factors. Weston<sup>1</sup> has pointed out that at least eighteen variables, the more important ones of which are temperature, composition of dilution water, dilution used, nitrification, interfering substances present in the sample etc., can influence this test. The cost and maintenance of 20°C incubator is another hindrance.

In view of these disadvantages a simpler method, known till recently as oxygen absorption test and based on the determination of oxidizable matter by permanganate under fixed conditions of temperature and time, was standardized. The determination of the amount of oxygen taken up by an acidified sample in 4 hr from N/80 potassium permanganate solution when maintained in a stoppered bottle at 27°C is one of the most important tests used for assessing the relative quantity of oxidizable matter in the sample. The term<sup>4</sup> 'permanganate value' is now recommended instead of 'oxygen absorbed in 4 hr'. This test<sup>5</sup> is commonly used for determining the strength of sewage or trade wastes and for measuring the effectiveness of sewage purification plants. Incidentally, this is the oldest chemical oxygen demand test<sup>6</sup>, a modification of which is used for detecting the rapidly oxidizable material by estimating the permanganate oxidized in 3 min. contact period. A number of other workers, however, choose 37°C for 3 hr, on the basis of an earlier observation that the figure obtained at 27°C for 4 hr is practically the same as that obtained at 37°C in 3 hr.<sup>7</sup> Experiments conducted in this laboratory also indicated the same 'Permanganate value' for these two test procedures (Table 1). It has been reported that effluents which have an oxygen-absorption value up to 10 mg/l and do not contain more than 1.5 mg/l of albuminoid ammonia almost always absorb less than 20 mg/l of dissolved oxygen in five days.<sup>8</sup> It is worth mentioning here that the Royal Commission standard for B.O.D. of a purified sewage

is 20 mg/l<sup>9</sup>, which bears a definite ratio to permanganate value for a particular type of waste or effluent.<sup>2</sup>

For carrying out the permanganate value test, a thermostatic water-bath is required for maintenance of constant temperature (27°C or 37°C), and also for a tropical country like ours the temperature of even 37°C is sometimes difficult to maintain in a thermostatic bath as temperatures over 40°C are frequently met during the summer months. In laboratory or pilot-plant investigations, even 3 hr permanganate value test is too time-consuming, which necessitated a still simpler and quicker test. It was noted that the total oxygen absorbed from the permanganate varies greatly

TABLE 1—PERMANGANATE VALUES AT 37°C FOR 3 HR AND AT 27°C FOR 4 HR

Sample	Permanganate Value (mg/l)		Deviation (mg./l.)
	3 Hr at 37°C	4 Hr at 27°C	
(a) Phenol Soln. prepared in the Laboratory (1)			
(i)	106	104	+2
(ii)	103	104	-1
(iii)	60	58	+2
(iv)	56	54	+2
(v)	53	55	-2
(vi)	48	48	Nil
(b) Weak Ammoniacal Liquor of Coke-Oven Plant at Sindri (2)			
(i)	255	255	Nil
(ii)	150	146	+4
(iii)	132	133	-1
(iv)	132	128	+4
(v)	116	113	+3
(vi)	106	105	+1
(vii)	74	72	+2
(viii)	66	66	Nil
(c) The Combined Effluent of the Sindri Factory (3)			
(i)	150	146	+4
(ii)	70	70	Nil
(iii)	70	64	+6
(iv)	56	56	Nil
(v)	53	49	+4
(vi)	50	50	Nil

N.B. (1) Phenol solution containing approximately 25 to 60 ppm. phenol.

(2) Weak ammoniacal liquor at Sindri containing free & fixed ammonia, sulfide, cyanide, phenols, pyridine, oils, etc.

(3) The combined effluent of the Sindri Works containing free & fixed ammonia, sulfide, cyanide, phenols, oils, etc.

with time and temperature, the concentration of the reagents and the intensity of light also affect the test.<sup>8</sup> The studies were carried out with the effluents of the Sindri Works of FCI Ltd., raw water, phenolic liquor, etc.

### Experimental Procedure

In view of the time interval of nearly 3 to 4 hr required for the permanganate value test, studies were made in the laboratory for standardizing a method requiring a shorter time and simpler equipment. The maintenance of any specific constant temperature required a thermostatic bath, and to make the test procedure still simpler the temperature of boiling water was chosen for study on 'permanganate value' test as this temperature is most easily obtained in a water-bath.

The experimental procedure is as follows: 100 ml. of a sample under test (or a properly diluted sample)

was taken in a 300 ml. stoppered bottle to which 10 ml. sulphuric acid (1 : 4) and 10 ml. N/80 potassium permanganate were added. The stoppered bottle was then put on a water-bath for various periods of time. The bottle was taken out which was cooled under running tap water. 10 ml. of 10 per cent potassium iodide was then added and after 10 minutes the liberated iodine was titrated against a dilute solution of sodium thiosulphate using starch as the indicator. A blank experiment was made with the reagents added to the distilled water and placed side by side in the boiling water-bath with the samples. The values thus obtained were compared with those obtained at 37°C for 3 hr (Table 2). It was observed that the 15 min. value thus obtained gave reproducible values and tallied remarkably with the values at 37°C for 3 hr. (Table 3)

It was also observed that an increase or decrease of time by 1 to 2 minutes does not affect the results. This method was later used satisfactorily by the authors<sup>10</sup> in

TABLE 2—PERMANGANATE VALUE AT BOILING WATER TEMPERATURE AT INTERVALS FROM 5 TO 30 MIN.

Sample	Permanganate Value (mg/l)					
	In boiling water temperature					3 Hr at 37°C
	5 min.	10 min.	12 min.	15 min.	30 min.	
Coke-Oven and Gas Plant Effluent (1)						
(i)	61	66	68	69	—	65
(ii)	167	171	—	173	—	172
Sulphate Plant Effluent (2)						
(i)	194	195	—	200	—	199
(ii)	83	—	86	101	—	94
Combined Effluent of the Sindri Factory (3)						
(i)	—	56	58	59	—	55
(ii)	56	58	62	62	—	57
Phenol Soln. Prepared in the Laboratory (4)	103	105	—	109	109	103
Weak Ammoniacal Liquor of Coke-Oven Plant (5)	101	110	—	113	119	110
Sodium Thiosulphate Soln.	82	81	—	83	90	82
Potassium Thiocyanate Soln.	97	103	—	104	105	104

N.B. (1) Coke-oven and gas plant effluent at Sindri containing free and fixed ammonia, water softener waste sludge, oils, cyanide, sulphide, etc.

(2) Sulphate plant effluent at Sindri containing free fixed ammonia, sometimes weak ammoniacal liquor also.

(3) The combined effluent of the Sindri Works containing free and fixed ammonia, sulphide, cyanide, phenols, oils, etc.

(4) Phenol solution containing approximately 60 ppm phenol.

(5) Weak ammoniacal liquor at Sindri containing free and fixed ammonia, sulphide, cyanide, phenols, pyridine, oils, etc.

the study of the biological treatment of phenolic liquors. It saved enormous time.

TABLE 3—PERMANGANATE VALUES AT BOILING WATER TEMP. FOR 15 MIN. & AT 37°C FOR 3 HR

Sample	Permanganate Value (mg/l)		Deviation (mg/l)
	15 minutes (boiling water temperature)	3 Hr. at 37°C	
(a) Raw Water (1)			
(i)	6	6	Nil
(ii)	6	5	+1
(iii)	5	5	Nil
(iv)	4	3	+1
(b) Coke-Oven and Gas Plant Effluent (2)			
(i)	89	87	+2
(ii)	89	91	-2
(iii)	69	65	+4
(iv)	62	56	+6
(v)	45	43	+2
(vi)	32	30	+2
(vii)	17	16	+1
(c) The Combined Effluent of the Factory (3)			
(i)	86	84	+2
(ii)	69	66	+3
(iii)	62	58	+4
(iv)	60	58	+2
(v)	59	55	+4
(vi)	21	20	+1
(d) Sulphate Plant Effluent (4)			
(i)	200	199	+1
(ii)	96	90	+6
(iii)	71	74	-3
(iv)	59	56	+3
(e) Phenol Soln. Prepared in the Laboratory (5)			
(i)	113	109	+4
(ii)	109	103	+6
(iii)	58	53	+5

(f) Weak Ammoniacal Liquor of Coke-Oven Plant (6)

(i)	161	155	+6
(ii)	113	110	+3
(iii)	73	66	+7

- N.B. (1) Raw water of the river Damodar collected near the discharge of the effluent of the Sindri Works.  
 (2) Coke-Oven and gas plant effluent at Sindri containing free and fixed ammonia, water softener waste sludge, oils, cyanide, sulfide etc.  
 (3) The combined effluent of the Sindri Works containing free and fixed ammonia, sulfide, cyanide, phenols, oils etc.  
 (4) Sulphate plant effluent at Sindri containing free and fixed ammonia, sometimes weak ammoniacal liquor also.  
 (5) Phenol solution containing approximately 30 to 60 ppm phenol.  
 (6) Weak ammoniacal liquor at Sindri containing free and fixed ammonia, sulfide, cyanide, phenols, pyridine, oils, etc.

### Acknowledgement

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# A Note on the Spectrophotometric Estimation of Biuret in Commercial Urea by Cobalt Biuret Complex Method

By

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A spectrophotometric method for estimating biuret, even in low amounts, in commercial urea based on the formation of a coloured complex with a cobalt salt has been reported.

A method for the estimation of biuret in the commercial urea has been developed by forming a coloured complex with cobalt salt. From a series of experiments it has been concluded that this method is suitable for the estimation of low percentage of biuret present in the commercial urea.

It is to be noted however that biuret forms coloured complex with Cu and Ni salts in presence of alkali.<sup>1</sup> The biuret content can be quantitatively estimated from the above two complexes and already there are some references in the literature to that end.<sup>2, 3</sup>

It has been found that a cherry red colour is developed when biuret is added to the Cobalt nitrate solution in presence of alkali followed by a few drops of 30 per cent hydrogen peroxide. This colour remains stable for a long time and obeys Beer-Lambert's law. It has maximum absorption at 500 m $\mu$  which is distinctly different from cobalt nitrate solution taken.

## Experimental

About 5 ml. of 30 per cent potassium hydroxide is taken in 100 ml. volumetric flask and 4 ml. of 5 per cent cobalt nitrate solution is added to it.  $\text{Co}^{++}$  is further oxidized to  $\text{Co}^{+++}$  state with a few drops of 30 per cent of hydrogen peroxide. The commercial urea containing biuret is then added to the mixture in 100 ml. volumetric flask and the flask is then filled up to the mark by distilled water.

The cobaltic complex obtained in the filtrate is then estimated spectrophotometrically by the usual way at  $\lambda$  max. 500 m $\mu$ . The standard graph is first drawn (Fig. 1)

with known percentages of biuret in urea and then an unknown percentage of it is estimated from the standard graph.

## Results & Discussions

Freshly prepared coloured solution of biuret cobalt complex behaves in accordance with the Beer-Lambert's law. Under standard conditions, the quality of the colour is always same, and the optical density determined by the spectrophotometer is directly proportional to the concentration (Table 1).

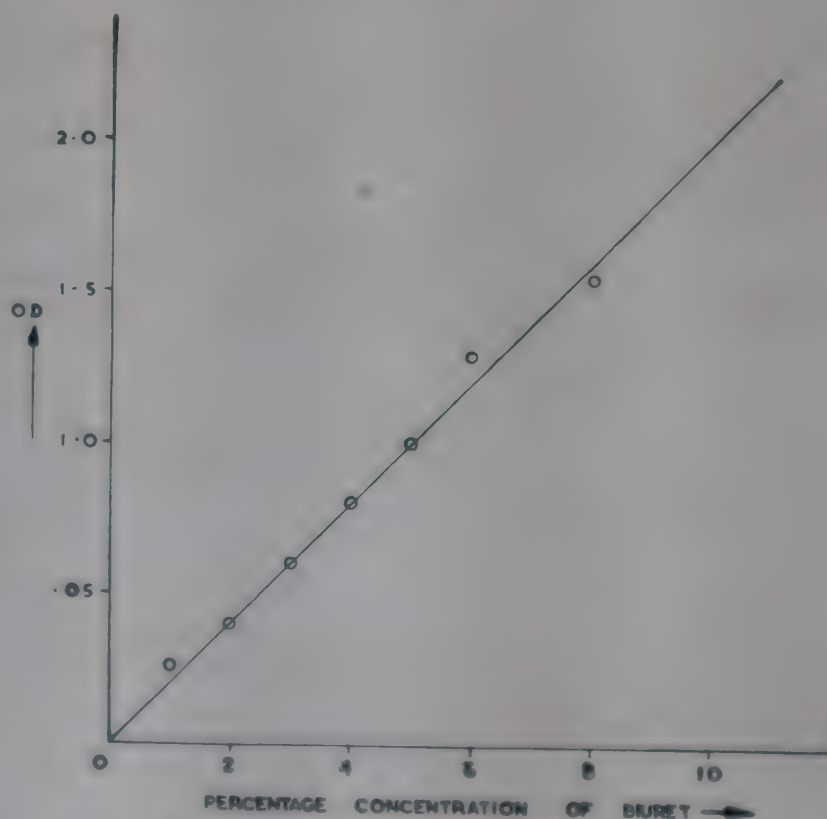


Fig. 1. Potassium Cobalt Biuret Complex at 500 m $\mu$ .

TABLE 1—POTASSIUM COBALT COMPLEX  
(Urea 30 g./l. containing different percentages of Biuret)

Wavelength, mμ	Sample No.	Percentage of Biuret taken	Optical Density	Percentage of Biuret from Standard Graph	Error
500	I	0.5	.011	0.53	+0.03
	II	2.5	.049	2.48	−0.02
	III	4.5	.084	4.20	−0.30
	IV	7.0	.134	6.75	−0.25
	V	Commercial	.030	1.50	

A comparative study of estimation of the different biuret complexes reveals some important facts. In the region of low percentage of biuret in urea, cobalt biuret complex method is found suitable for estimation.

Further work has been done and will be communicated shortly.

#### Acknowledgements

The authors' thanks are due to Dr. K. R. Chakravorty, General Manager, for encouragement and to Dr. B. K. Banerjee, Deputy Superintendent, P & D Division, for help and guidance throughout the progress of the work. Thanks are also due to Sri K. C. Banerjee, Asst. Supdt., for showing interest in this work.

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# Technical Digests

## Corrosion-Inhibitor from Coke Oven Sludge

Dilute sulphuric acid is used extensively for descaling, pickling and general cleaning of steel and other ferrous alloys. During such treatments, corrosion-inhibitors are used to minimize the attack of the acid on the alloys or metals.

A method\* has been developed at the Planning & Development Division of FCI for inhibiting corrosion of steel from the acid sludge obtained as a waste material in the purification of crude benzol.

The crude benzol, obtained as a by-product in a coke oven plant, is purified by washing with sulphuric acid. This purification gives rise to the formation of a foul-smelling, viscous, black sludge. In the process\* developed here, a profitable use of this sludge has been found out. The acid sludge is heated to remove a substantial portion of residual benzole and thickened. The mass is then cooled and to it dilute sulphuric acid is added. The sulphuric acid extract is used as a corrosion-inhibitor.

The process is as follows: 150 g. of the acid sludge is heated at 70°-100°C for about 40 minutes to remove a substantial portion of the residual benzole and for thickening the mass. The mass is then cooled to about 40°C, and 50 ml. of sulphuric acid (98 per cent diluted with an equal volume of water) is added to it and kept at the room temperature for several hours. The mass separates out into two portions i.e. a thick jelly-like semi-solid mass and an easy flowing acidic liquor. The latter is poured off. It constitutes the corrosion-inhibitor.

Another corrosion-inhibitor has been developed† from the same coke oven acid sludge using hydrochloric in place of sulphuric acid. The process is as follows: coke oven acid sludge is heated for about 10-40 minutes at 70°-100°C to remove substantial amount of the residual benzol and also to thicken the mass. The viscous mass

is cooled to 40°C and about 40 ml. of hydrochloric acid (Sp. gr. 1.16) are added to it. It is kept at the room temperature for several hours, when it separates out into two layers, viz., a jelly-like semi-solid mass and an easy-flowing acidic liquor. The latter is poured off. Its inhibitive effect is enhanced by adding urotropine into it.

## Active Carbon from Lignite

The use of active carbon for refining sugar, edible oils and fats, for the removal of disagreeable flavour, 'aste, odour and colour from many food products, alcoholic beverages and potable water, etc. and as a catalyst or catalyst-carrier in various reactions, is well-known. A number of carbonaceous materials, viz. wood, sawdust, peat, lignite and pulp-mill waste, etc. can be used for its production.

A process for the preparation of active carbon from Indian lignite‡ and molasses has been developed in this laboratory of the FCI. It comprises the following procedure: Lignite is air-dried and crushed to a fine powder, and then blended with about half or three-fourth of its weight of molasses. Prior to mixing, adequate water is added to the molasses so that the blended product makes a paste, which is then extruded or granulated to a size 2 to 10 mm. The sized material is then dried at 100°C and carbonized, followed by activation either in a fixed or dynamic bed. In a fixed bed the mass is carbonized and activated by a mixture of steam and air at 600°-900°C. While using a dynamic bed, the fuel gas is burnt in a furnace and hot flue gas is passed through an activation chamber. At a chamber temperature of 600°C, the blended material is charged and then carbonized (550°-700°C) by hot flue gases. After carbonization, activation is done by a mixture of superheated steam and flue gas for 1-4 hr in the temperature range of 600°-900°C. When activation is over, the product is quenched in water in an atmosphere of nitrogen, treated with acid, then washed and dried.

In a slight variation of the process, the crushed air-dried lignite of 2-10 mm. size is soaked in an aqueous solution of molasses of sp. gr. 1.1-1.45.

‡ 'A Process of Preparation of Active Carbon from Indian Lignite & Molasses'. Indian Pat. No. 60287. (Inventors: Dr. K. R. Chakravorty, S. P. Sen, B. Chattopadhyaya & S. Chatterjee).

\* 'Process for Preparing from Coke Oven Acid Sludge a Liquor that Inhibits Corrosion of Steel in Sulphuric Acid.' Indian Pat. No. 73949 (Inventors: A. K. Roy, A. Mukerjee & Dr. K. R. Chakravorty).

† 'Process for Preparing from Coke Oven Sludge a Liquor which Inhibits Corrosion of Steel in Hydrochloric Acid.' Indian Pat. No. 73950 (Inventors: A. K. Roy, A. Mukherjee & Dr. K. R. Chakravorty).

The active carbon obtained by this process is far more reactive than in the case from raw lignite alone without molasses treatment. The reactivity of the product is comparable with that of the high grade imported product.

### Fertilizer Project at Gorakhpur

In accordance with the recommendations of the Fertilizer Technical Committee of the Government of India for setting up a fertilizer unit at Gorakhpur (U.P.) based on petroleum naphtha from Barauni refinery, the Government of India entrusted this work to the FCI Ltd. in the middle of 1961 (Fig. 1). The development council specified that this unit should have an annual capacity of 70,000 tons of nitrogen as urea. The Government later recommended a 10 per cent extra capacity in ammonia production and specified a capacity of 80,000 tonnes of nitrogen. A detailed project report was, therefore, drawn at the Planning and Development Division, based on which the plant has been designed.

On the above basis, the annual production of urea will be 1,73,920 metric tons for which ammonia requirement will be 1,04,700 metric tons. After providing an extra capacity of 10 per cent in ammonia plant and assuming 330 working days in a year, the capacity of the ammonia plant would be 350 Te/day, which means the rated capacity of urea plant is 543.5 Te/day.

After consulting various departments of the Central and State Governments, including the Ministry of Defence, the present site, situated about 4 miles north of the city, has been finally selected. The site is well-connected with the city by two pucca roads and a railway line, and has enough resources of water, viz. from a nearby perennial river (*Rohin*) and a lake (*Chilwa*) which does not dry up in summer. Water for potable and sanitary purposes will be available from tube wells.

The raw material for the production of ammonia will be naphtha (fraction upto about 150°C) from the refinery at Barauni—210 miles from Gorakhpur—in railway tank cars. Its annual requirement would be of the order of 87,600 metric tons for which a storage arrangement for 8,500 tons would be provided at the works site.

In the process, naphtha will be gasified under pressure with oxygen using the non-catalytic partial oxidation process. The carbon soot in the raw gas will be removed by scrubbing with water and recovered from the slurry by washing with the fuel oil and then pelleted. These pellets will be used as fuel in the boilers for

steam generation in addition to coal. The gases, comprising hydrogen, carbon dioxide and carbon monoxide from the gas generators, will be cooled in a waste heat boiler and the heat in the gases will be recovered as steam. Carbon monoxide in the raw gases will be 'shifted' to carbon dioxide giving additional hydrogen. While carbon dioxide will be removed by scrubbing with hot potash solution and subsequently with amine solution, the residual carbon monoxide will be removed by washing with liquid nitrogen. The tail gases from the liquid nitrogen wash section containing carbon monoxide, hydrogen and nitrogen will be used as fuel gas for heating the driers in the urea plant, and the excess will be used in boilers. The purified gases containing nitrogen and hydrogen will be compressed to 350-400 kg/cm<sup>2</sup> and sent for ammonia synthesis (Fig. 2). The unconverted gas after separation of ammonia will be recirculated along with fresh make-up gas. The liquid ammonia and the carbon dioxide gas recovered from the CO<sub>2</sub> removal system will be compressed and sent to the urea plant where these will be passed through a reactor (or autoclave) working at a pressure 180-230 kg/cm<sup>2</sup>. The urea synthesis will work in four-streams, while decomposition, evaporation, crystallization, drying, prilling and cooling will be done in two streams (Fig. 3).

The pattern of the utilities will be as follows:

- (i) *Electricity*: About 40,000 kVA available from the U.P. Government's super-grid, which will be stepped down at the factory's substation.
- (ii) *Fuel*: For the generation of process steam, coal in the beginning from Jharia and Karanpura coalfields (Bihar) until it is available from Singrauli area (Mirzapur Dt. U.P. and the adjoining area of M.P.) will be used.
- (iii) *Steam*: Taking into consideration the requirements of ammonia and urea plants, water treatment and miscellaneous other services, the normal continuous rating of steam generation plant shall be 90 tons/hr.
- (iv) *Cooling Water*: Approximately 15,300 m<sup>3</sup>/hr of cooling water will be in circulation for which 1,000 m<sup>3</sup>/hr of process water will be required for replenishment to compensate losses.
- (v) Water for sanitary, residential and fire-extinguishing purposes will be 285 m<sup>3</sup>/hr.
- (iv) *Feed Water for Boiler & Process Units*: Requirements are 90 tons/hr and 10 tons/hr respectively.



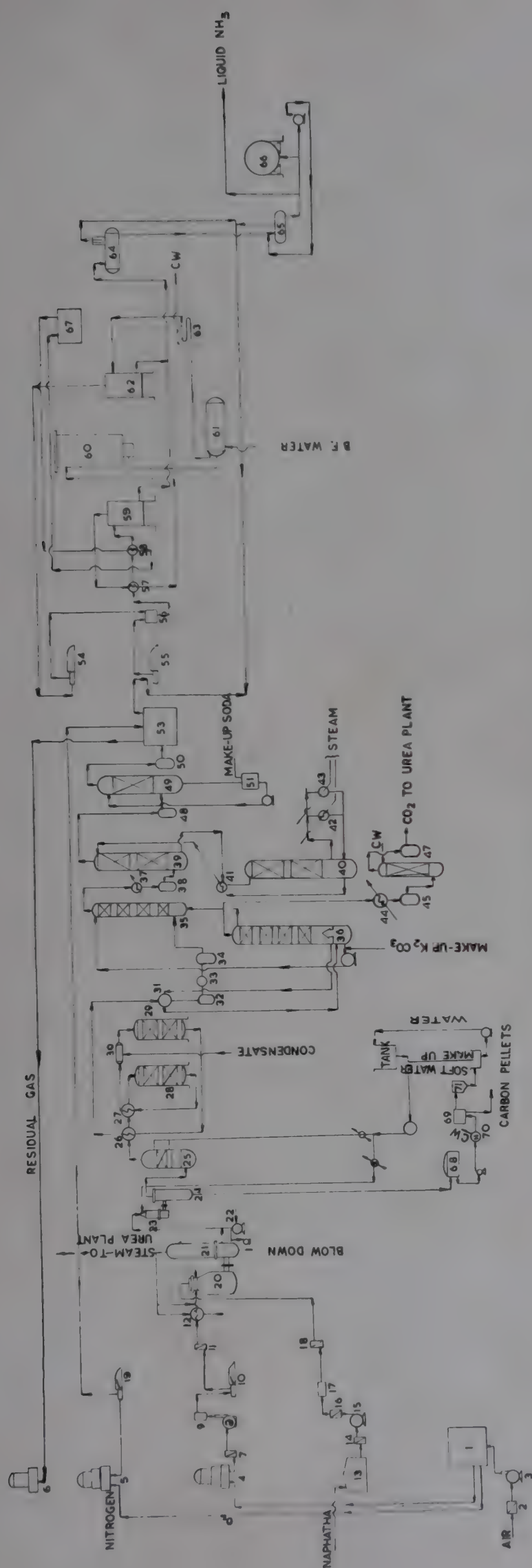


Fig. 2. Flow Diagram of Ammonia Plant.

### Legend

1. Air Separation Unit
2. Air Filter
3. Air Compressor
4. Oxygen Gas Holder
6. Residual Gas Holder
5. Nitrogen Gas Holder
7. Oxygen Filter
8. Oxygen Booster Pump
9. Filter
10. Oxygen Compressor
11. Compressed Oxygen Filter
12. Oxygen Heater
13. Naphtha Storage Tank
14. Filter
15. Naphtha Booster Pump
16. Filter
17. Naphtha Charge Pump
18. Filter
19. Nitrogen Compressor
20. Reactor
21. Waste Heat Boiler
22. B. F. Water Pump
23. Quench Vessel
24. Carbon Slurry Separator
25. Water Scrubber

26. Heat Exchanger
27. Heat Exchanger
28. 1st Shift Conveyor
29. 2nd Shift Conveyor
30. Water Quench Vessel
31. Heat Exchanger
32. Separator
33. Heat Exchanger
34. Separator
35.  $K_2CO_3$  Regenerator
36.  $K_2CO_3$  Regenerator
37. Heat Exchanger
38. Separator
39. M. E. A. Absorber
40. M. E. A. Regenerator
41. Heat Exchanger
42. Steam Heater
43. Steam Heater
44. Heat Exchanger
45. Separator
46.  $CO_2$  Scrubber
47. Separator
48. Separator
49. Soda Scrubber
50. Separator

51. Soda Tank
52. Soda Pump
53. Liquid Nitrogen Washing Unit
54. Recirculator
55. Synthesis Gas Compressor
56. Oil Filter
57. Cold Exchanger
58.  $NH_3$  Cooled Condenser
59. Secondary Separator
60. Ammonia Converter
61. Waste Heat Boiler
62. Primary Separator
63. Trombone Cooler
64. Let Down Tank
65. Liquid Ammonia Weighing Scale
66. Ammonia Storage Tank
67. Refrigeration Unit
68. Flash Tank
69. Pelletizing Unit
70. Heat Exchanger
71. Surge Vessel
72. Heat Exchanger
73. Heat Exchanger

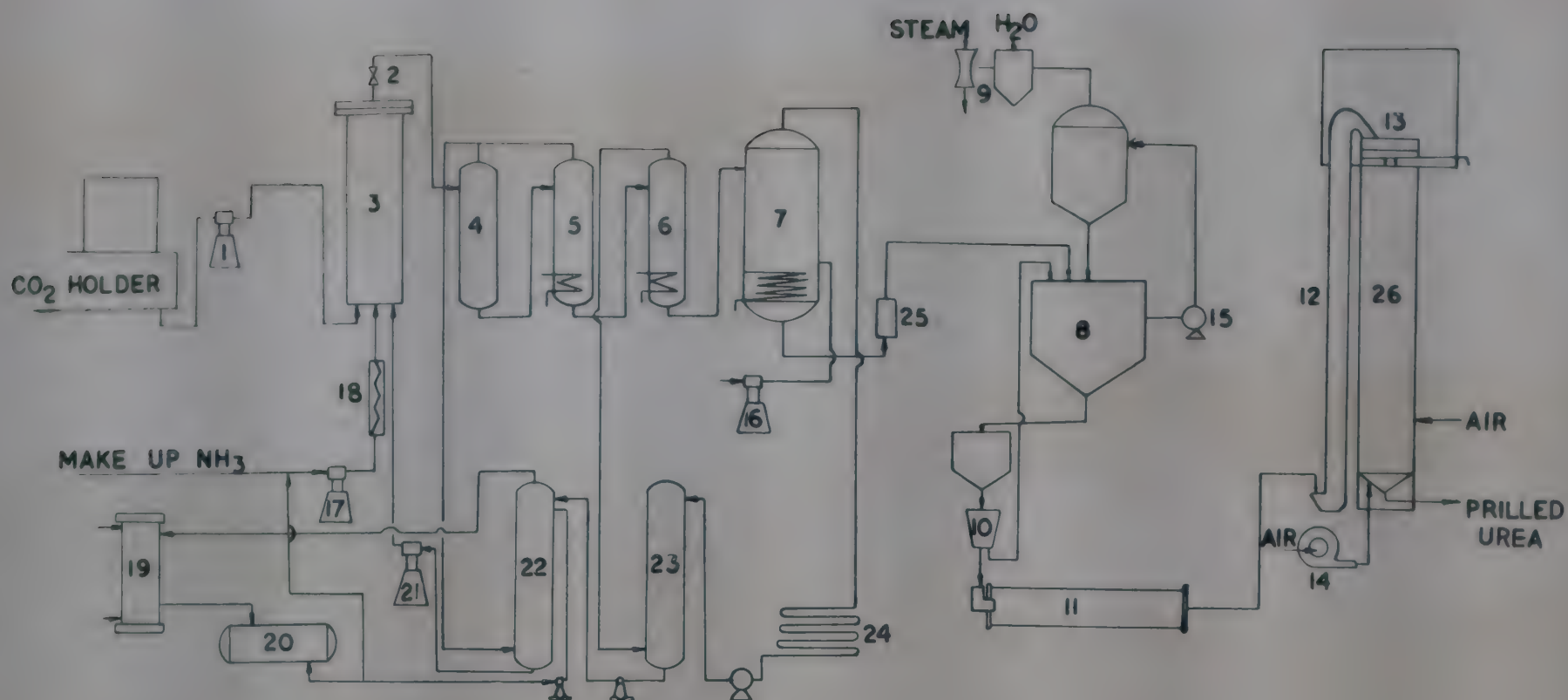


Fig. 3. Flow Diagram of Urea Plant.

### Legend

- |                                   |                              |                                    |
|-----------------------------------|------------------------------|------------------------------------|
| 1. CO <sub>2</sub> Compressor     | 10. Centrifuge               | 19. Ammonia Condenser              |
| 2. Let Down Valve                 | 11. Dryer                    | 20. Liquid Ammonia Reservoir       |
| 3. Autoclave                      | 12. Bucket Elevator          | 21. Solution Feed Pump             |
| 4. High Pressure Decomposer No. 1 | 13. Melter                   | 22. High Pressure Absorber         |
| 5. High Pressure Decomposer No. 2 | 14. Air Blower               | 23. Low Pressure Absorber          |
| 6. Low Pressure Decomposer        | 15. Circulating Pump         | 24. Gas Condenser                  |
| 7. Concentrator                   | 16. Air Compressor           | 25. Concentrated Urea Soln. Filter |
| 8. Crystalliser                   | 17. Liquid Ammonia Feed Pump | 26. Prilling Tower                 |
| 9. Condenser and Ejector Set      | 18. Ammonia Preheater        |                                    |

## Ammonia Synthesis Reactor

Two methods of removing the heat of reaction of the ammonia synthesis reaction are possible, viz. (1) the direct removal by means of heat exchanger within the reactor, and (2) the injection of cooled feed to the main stream of gases passing through the reactor catalyst bed. The former is considered better by the author [W. Hennel, *Brit. Chem. Engng.*, 9 (1964), 290-293], who has described a number of constructions, each employing an extended surface heat exchanger fitted within a reactor, which were shown entirely successful in practice.

Using the kinetic equation of Blasiak and data from an earlier comparison made by Baumann and Misek using the Tiemken-Pyzov equation, a graph has been obtained which indicates that to obtain a given percentage of ammonia in the outlet gases, less catalyst is required by using a built-in heat exchanger in the catalyst bed instead of direct removal of heat by cooled gas.

There are two causes for the reduced output of reactors in which heat of reaction is removed directly. One is that a large fraction of the reactants bypasses the first layers of the bed where the reaction velocity is greatest, this fraction reacting in the bottom layer with a considerably reduced velocity. The other cause is the non-uniform distribution of temperatures, which increase with the length of the individual catalyst layers. Although the heat exchanger tube takes up a certain amount of internal space in the reactor, the reduced quantity of catalyst required while using built-in heat exchanger more than offsets the above disadvantage. The author has discussed problems of heat exchanger design if it is to be embedded in catalyst layers. According to him the heat exchange ratios in the classical NEC reactor are inadequate. His design consists of flat pipes, called 'fins', connected to a collector from where the gas can be led to a main central pipe and thence to top of catalyst bed. Detailed drawings are given for 760 mm diam. heat exchanger. He claims that operating experience since 1959 has shown

that a converter with such a heat exchanger is thermally highly stable and gives adequate heat exchange to obviate overheating of catalyst.

The problems of design of gas-gas heat exchanger for heating inlet gas to converter have also been discussed, e.g. a design in which higher gas velocity is obtained by dividing the exchanger tubes into two bundles connected in series. It is claimed that such a construction reduces the size of the exchanger compared earlier designs. The use of AISI 304L, AISI 321 or AISI 347 for construction of converters has been recommended, and according to the author the experience gained at the Nitrogen Works, Kedzierzyn (Poland), shows that only austenitic chrome-nickel steel with carbon content below 0.80 per cent gives a satisfactory corrosion-resistant interior of ammonia synthesis reactors.

## Gas from Light Petroleum Products

The use of liquid petroleum products for town gas manufacture extends back over 90 years when carburetted water gas was first introduced. Initially light petroleum fractions were used for carburetting, but with the advent of the internal combustion engine a higher boiling fraction, distilling between kerosene and lubricating oil, was employed.

In the last decade the proportion of gas obtained from oil has increased to nearly 24 per cent in U.K. due to the following circumstances: (i) siting of oil refineries near the centres of consumption in Europe resulting in a wide range of petroleum products made available, (ii) the decreasing differential between coal and oil prices and the lower capital and labour requirements of oil gasification plants, (iii) the increasing problem of disposal at economic price of coke which represents a higher proportion of the thermal yield from the carbonization of coal than does gas, and (iv) the development of cyclic catalytic oil gasification processes with higher conversion efficiencies.

By 1958 light petroleum distillate became established as a feed-stock for gas making,

and its increasing availability arises from the increased demand for middle distillates for aviation fuel, diesel fuels for road transport and heating fuel. To meet these demands more crude is processed in U.K. refineries, yielding a light fraction, which, although in the motor spirit range, is unsuitable on account of its low octane rating. But for gas-making this light fraction is preferable to the heavier feedstocks by virtue of its low sulphur content and low carbon to hydrogen ratio. New processes, based specifically on the use of light oil, have been developed and the scope of existing processes has been increased. With the replacement of gas oil by light distillates not only has a relatively expensive raw material in short supply been replaced by a cheaper feedstock, but numerous technical advantages have accrued. The product is more compatible with coal gas in that the hydrogen content is increased and the specific gravity and carbon monoxide content are reduced. In addition to an increase in output of 26 per cent there is a reduction in the therms deriving from coke which is an advantage since the coke-based therm is now more expensive than the oil-based therm.

Another petroleum fraction of increasing importance is liquefied petroleum gas (LPG), which can be used for direct enrichment of lean gases and can be stored in the liquid state under moderate pressure or a mild refrigeration. The North Thames Gas Board at Southal has established in 1963 a continuous oil gasification plant to reform LPG from a nearby Esso refinery. The U.K. Government has also approved of the Gas Council's scheme for the importation of liquefied natural gas from Sahara.

In the first half of the last decade cyclic catalytic gasification plants of the Onia-Gegi and Segas type were established at the existing carbonizing plants, but from 1958 onward larger units were sited near refineries and operated at high load factor. The advantages of cyclic catalytic process are its ability to handle a wide range of feedstocks, to produce gas economically

in small units and to manufacture a 500 Btu/ft<sup>3</sup> gas in a single stage.

In the Shell gasification process the intimate mixture of the hydrocarbon feedstock with oxygen and steam is fed to the reactor. The mechanism of gasification may be considered as taking place in two stages, the principal products being carbon monoxide and hydrogen of which the former is 'shifted' to hydrogen. This process is capable of gasifying a wide range of feedstocks at high thermal efficiency, but is capital-intensive.

The features of the two units for the reformation of LPG by Otto process are their ability to be rapidly brought on steam and their automatic control and shut down to safety in the event of any failure.

In comparison with LPG, the lower cost, greater availability and easier storage of light distillate makes it the preferred feedstock for seasonal loads. The chemical industry till 1962 produced synthesis gas by the continuous catalytic reforming of natural gas and LPG when ICI announced their new process, now in operation in Heysham and Billingham, for continuous reforming of light distillate at pressure with moderate steam-to-oil ratio. With liquid hydrocarbon containing components higher than C<sub>4</sub> there is the possibility of laying down carbon on the catalyst when reforming to a hydrogen-rich gas at pressure. This tendency may be overcome by using a large excess of steam but this is uneconomic. The solution by ICI lies in the development of a special catalyst which promotes the steam-carbon reaction and maintains its activity over a long period.

As far back as 1957, a 2-stage continuous process for the production of town gas from light distillate by steam reforming in the presence of a highly active nickel catalyst at 25 atm was developed at the Midlands Research Station of the Gas Council. In this process, by converting the light distillate to a methane-rich gas at 500°C carbon deposition is avoided. The first stage of this process is slightly exothermic and requires only a simple reactor with a packed bed of catalyst, and the rich gas so obtained may be reformed autothermically over a conventional nickel catalyst in a second simple reactor. If the rich gas from stage 1 is used to enrich the lean gas from an ICI reformer, this combination of the two processes in parallel produces town gas entirely from light distillate. This combination process,

TABLE 1—TOWN GAS FROM LIGHT DISTILLATE BASED ON THE ENRICHMENT OF 10 MILLION SCFD OF LEAN GAS

Composition	Town Gas after Partial CO <sub>2</sub> Removal & Enrichment by			
	Lean Gas	Gas Council Catalytic Rich Gas	Gas Council Gas Recycle Hydrogenation	Commercial Butane
CO <sub>2</sub>	20.0	14.1	13.3	13.9
H <sub>2</sub>	69.0	48.6	55.9	68.5
CO	5.0	3.3	5.5	5.0
CH <sub>4</sub>	6.0	33.8	17.9	5.95
C <sub>2</sub> H <sub>6</sub>	—	—	7.0	—
C <sub>2</sub> H <sub>4</sub>	—	—	0.4	6.65
C <sub>4</sub> H <sub>10</sub>	—	—	—	—
N <sub>2</sub>	—	0.2	—	—
C.V.	295	500	500	500
S.G.	0.434	0.469	0.476	0.476
Flame Speed Factor	56.6	35.1	39.9	46.5
Final Gas Output, mscfd	10.0	16.98	9.97	10.07

[Cribb, G. S., Brit. Chem. Engng., 9 (1964), 366-370]

also developed at the Midlands Research Station, is known as Gas Council Gas Recycle Hydrogenator (GRH). The author has given a comparison of the two methods of enriching lean gas from an ICI reformer (Table 1).

#### Nitric Acid Manufacture

The \$1.5 m. new 280 short tons/day nitric acid plant at Yazoo City, Missouri, of Mississippi Chemical Corpr., designed and erected by D. M. Weatherly Co., is notable for its high ammonia-conversion efficiency. The major advantages are: low initial capital cost, say about 30 per cent lower than the conventional low-pressure system; an overall nitrogen recovery rate as high as 95 per cent in the form of nitric acid of 57 per cent concentration relative to ammonia fed to the process.

The conversion efficiency in the ammonia converter is around 97 per cent and the absorber operates with an overall efficiency as high as 99 per cent. The efficient performance is largely due to (i) thorough mixing of the ammonia-air feed stream, (ii) high purity of the feedstream, (iii) careful control of mixture temperature and composition in the converter, and (iv) good absorber efficiency.

The anhydrous ammonia in liquid form is vaporized and then superheated at about 350°F by process steam and transferred at 180 psi to an ammonia/air mixer with the air supply centrifugally compressed to

approximately 120 psi and heated to over 500°F by heat exchange with the in-process nitrogen oxides stream. The ammonia and air streams, compressed and heated, pass to a double mixing operation based on orificing.

The purity of the ammonia-air stream is due largely to the design of the gas-handling system, including piping and air filter being fabricated of alloy steel—Type 304. The mixed air and ammonia vapour enters a converter, passing over a platinum gauge catalyst where the ammonia burns to form nitrogen oxides at 1680°F. The life of the platinum gauge is 900-1000 hr.

[Nitrogen, (1964), 29, 30-31]

The Tennessee Valley Authority has modified its existing pressure nitric acid plant manufacturing at present 58 per cent acid to obtain 62.5 per cent acid without loss of nitric oxides. Some of the changes made in the original unit are (i) addition of another acid bleacher, (ii) feeding of hot air and nitrogen oxides leaving this bleacher into the end of the second pass of the cooler condenser, (iii) installation of more efficient cyclone separators after the first, second and sixth passes of the cooler condenser, (iv) the existing separator, fitted after the fourth pass modified to operate more efficiently, (v) addition of a pump between the cooler condenser, acid receiver and the feed plates of the tower, (vi) the extension of the acid pipeline to allow acid to be added to either the seventh,

eighth, sixteenth, twentieth or twenty-first tray of the absorption tower and the addition of 12 more trays to the column.

The modification of the separators and the installation of the pump eliminated an entrainment loss at the separators and reduced the dilution of the product acid caused by the introduction of weaker acid carried over in the gas stream from the cooler condensers. These alterations have resulted in the nitrous gases being present in the absorption tower in their most reactive state and in a stronger acid being produced.

[*Ibid*, 36]

#### Australia's New Ammonia Complex Plant

The £6 million ammonia complex of ICIANZ Ltd. at Botany (Sydney) consists of an ammonia, a methanol and a urea plants and plants for producing nitric acid and prilled ammonium nitrate. The prilling technique gives greater flexibility of control over the type of product made enabling it to be produced in any form required.

The nitric acid plant uses the Du Pout process which operates at about 8 atmospheres pressure. Its main steps are: (1) oxidation of ammonia to NO, (2) oxidation of NO to NO<sub>2</sub> and (3) absorption of NO<sub>2</sub> in water to form HNO<sub>3</sub>. The oxidation of ammonia in air takes place autothermally over a platinum iridium catalyst (0.003 in. diameter wire gauge) at 900°C. The converted gases leaving the catalyst are cooled by heat exchange with the incoming air.

The oxidation of nitric oxide in the gases takes place in a serpentine type cooler condenser. Nitrogen dioxide formation is assisted by the pressure in the system and by low temperatures. While cooling, much of the water formed during the oxidation of the ammonia is condensed out in the form of a nitric acid solution containing about 40 per cent HNO<sub>3</sub>, which after collection is passed to the absorption section.

The absorber consists of a bubble-plate column with cooling coils on each tray. Cooling assists absorption; it is also required to ensure that the reconversion of nitric oxide, evolved in the process of absorption, back to nitrogen dioxide proceeds at a reasonable rate. High pressures in the absorber assist both the absorption and the reconversion reaction. The product nitric acid is usually controlled at around 55-60 per cent HNO<sub>3</sub>, and the dissolved oxides of nitrogen are removed in a 'bleacher' using warm air.

The ammonia nitrate production consists of (a) neutralization of 55-60 per cent nitric acid with ammonia to produce a solution containing around 80 per cent ammonium nitrate; (b) concentration of this solution to about 95 per cent ammonium nitrate; (c) prilling of the 95 per cent solution to give small spherical particles of ammonium nitrate, and (d) drying, cooling and coating the solid product. The design of the neutralisation step was carried out by ICIANZ, but the basic design of the subsequent steps was obtained from the Chemical Construction Corporation.

The urea plant is based on the process developed by the Dutch State Mines. Ammonia and carbon dioxide are reacted together at elevated temperature (200°C) and pressure (200 ats.) to form ammonium carbamate which then dissociates partially into urea and water. The biuret content in this urea is low (less than 0.3 per cent). Humphrey & Glasgow Ltd. was awarded the contract for the complete engineering of the production plant and for the associated storage and bagging facilities.

The ammonia synthesis plant employs the high pressure steam-reforming of naphtha developed by ICI. The basic process routes are as follows (1) Naphtha reforming (ICI process), (2) CO conversion, (3) CO<sub>2</sub> removal (Vetrocoke process), (4) Compression, (5) Methanol synthesis-Purification, (6) CO removal and (7) Ammonia synthesis.

The liquid naphtha, freed of sulphur by passing the vaporized naphtha mixed with hydrogen successively over beds of zinc oxide, cobalt, molybdenum and zinc oxide catalysts is mixed with superheated steam and fed to the primary reforming furnace containing vertical tubes packed with catalyst, forming hydrogen, CO, carbon dioxide and residual methane. In the secondary reformer, which serves the purpose of raising the temperature to reduce the methane content, and adding the necessary nitrogen for ammonia synthesis, the reacting gases from the first are treated over a bed of catalysts with air.

[Austral. Chem. Proc., 17 (1964), 7, 20-31]

#### Soil Testing in Fertilizer Use

For advising the farmer on the use of fertilizers, one must know what quantities of plant nutrients the expected crop would need and how much of this would be obtainable from the native soil sources.

Soil testing consists of collection of a representative sample of the field soil and determination of its fertility levels. A soil sample after having been properly recorded is analysed for the following, soil reaction (pH value); salinity; organic carbon; available phosphorus; available potassium.

Soil reaction is a decisive factor for crop growth. A good crop can grow within a certain range of soil pH. At the different soil testing laboratories of India, suitable pH ranges for different crop have been worked out extensively.

The soil salinity indicates the level of soluble salts present in the soil. Excessive quantities of such salts make the soil unsuitable for crop growth. The amount of organic carbon present is an indirect estimation of soil nitrogen reserve. From studies carried out both in pot culture and field experiments, a close relation has been found between the organic carbon contents of a soil and the yield of wheat, which is significant; lower the percentage of carbon, the lower the yields.

Normally most of the soils contain a considerably large reserve of phosphorus, but all phosphorus is not available to a growing crop. For determining minute quantities of available phosphorus, the photo-electric calorimeter is used. When a soil test reports that the soil contains 50 lb of available phosphorus, it does not mean that is the only quantity of phosphorus a crop can get from the soil. It indicates only the rate of supply per acre but not the time rate, which is the probability of a crop showing response to phosphatic fertilizers.

Unlike available phosphorus, all potassium determined as available potassium in soil test is really available to a growing crop. When the rate of replenishment of available K is quite fast, soil analysing low in available potassium may maintain good crop growth with potassic fertilizers.

Soil testing, thus, aims at assuring an optimum soil fertility to the growing crop. There are no soil test and plant yield correlations to calculate quantities of N, P and K to get so many pounds of grains. Soil testing indicates only one factor controlling crop growth and that is soil fertility.

[Fertilizer News, 9 (1964), 9, 9-14]

#### Marine Gypsum for Fertilizer Manufacture

Gypsum can be precipitated from sea

water brine (15° Be) from solar salt works by the addition of waste distiller liquor (containing excess calcium carbonate) from soda ash plants. S. K. Raman & S. Diwakar Rao [Research & Industry, 9 (1964), 187-188] precipitated gypsum by the addition of 8 per cent calcium carbonate liquor in stoichiometric ratio to a synthetic solar brine. The precipitated gypsum was filtered under vacuum, washed with distilled water and dried.

The reactivity of this gypsum as well as natural gypsum was studied in a batch stirred vessel using ammonium carbonate (3000 g/l) solutions and taking reactants in the mole ratio at temperatures 40°, 50°, 60° and 70°C. The rates of formation of sulphate ions were studied under the same conditions of temperature, concentration and mole ratios of the reaction mixture in both cases. The kinetic data was obtained by estimating the concentration of  $\text{SO}_4$  ions in the solution against time of progress of reaction. A second series of experiments were done by completing the reaction to the extent of 98 per cent dissolution of gypsum, and the filtrate from the reaction slurry was evaporated and ammonium sulphate was crystallized under conditions of temperature-concentration prevalent in industrial operation.

The study has indicated that (i) the use of precipitated gypsum from sea-brine is technically feasible and will not be less in reactivity than the natural gypsum; (ii) the precipitated gypsum does not require the conventional calcination and grinding as in the case of natural gypsum since the former has a size less than 100 mesh; (iii) the chloride impurity of the precipitated gypsum can be lowered below the permissible limit of 0.2 per cent if the filter cake is repulped with water to a 30 per cent slurry, filtered and dried. Such gypsum could be used singly or mixed with the natural gypsum in the manufacture of ammonium sulphate.

#### Pyrophosphate as Fertilizer

The value of pyrophosphate as a source of plant nutrient has been studied by C. D. Sutton and S. Larsen [Abstr. Fertilizer News, 9 (1964), 8, 21]. The hydrolysis of pyrophosphate in soil was found to be largely an enzymatic process and the half life in days could be predicted from an equation. Studies on the uptake of pyrophosphate from soil by rye-grass indicated that in the sandy loam the half life predicted was 30 days. Water culture experiments on barley showed that pyro-

phosphate could act as a source of phosphate where possibility of hydrolysis in solution was excluded. The results indicated that pyrophosphate was not taken up so rapidly as orthophosphate under these conditions. The ratio of relative uptake of phosphorus from orthophosphate to that of pyrophosphate was found to be  $2.41 \pm 0.26:1$ . From uptake data obtained at various pH levels, the difference observed between the P uptake from pyro and orthophosphate are ascribed to the valencies of their component ions.

#### Cotton's Uptake of NPK

From manurial experiments conducted at Indore, it has been found that there is a slight increase in the absorption of phosphate when plants were fertilized with varying doses of nitrogen. This determination led to the discovery of the rate at which the three important nutrients were absorbed from the soil if the plants had grown normally and if none of the minerals was low and insufficient. It was observed that N : P : K ratio generally fluctuated between 3.3 : 1 : 3.3 to 3 : 1 : 3. It was later found that every gram of dry matter of the cotton plant as a whole contained nearly 14 to 16 mg. of nitrogen, 5 to 6 mg. of phosphoric acid and 14 to 16 mg. of potash under the rainfed as well as irrigated conditions.

A complex experiment consisting of all combinations of three levels of nitrogen (0, 30 & 60 lb.), three levels of phosphate (0, 100 & 200 lb.  $\text{P}_2\text{O}_5$ ) and three levels of potash (0, 100 & 200 lb.  $\text{K}_2\text{O}$ ) and the N : P : K ratios were determined in all the 27 treatments. The average N : P : K ratio at the zero level and at the 30 lb. level of nitrogen was found to be about 2.4 : 1 : 2.5 indicating sufficiency of phosphate and deficiency of nitrogen and potash. However, at 60 lb. N level, the ratio became almost normal, the mean of nine treatments being 3.1 : 1 : 3.1.

These results apparently suggested that any divergence from the normal N : P : K ratio of 3 : 1 : 3 would indicate deficiency of one of the three nutrients.

#### Fertilizer Production in Fourth Plan

It has been estimated that fertilizer requirements by the end of Fourth plan i.e. 1970-71 will be as follows: nitrogen 2.00,  $\text{P}_2\text{O}_5$  1.00 and  $\text{K}_2\text{O}$  0.35 million tons. At the time of finalization of the Third Plan the consumption of nitrogen and  $\text{P}_2\text{O}_5$  was estimated at 1.0 and 0.4 million

tonnes by the end of the plan.

In a note entitled "Pattern for Fertilizer Production in the Fourth Five Year Plan" issued by the Union Ministry of Food & Agriculture, the requirements of fertilizers for the different States have been worked out taking into consideration the recommendations for different crops (Table 1). The percentage of the area to be fertilized is based on the Third Plan targets of consumption, present levels and trends of fertilizer consumption during the past few years and fertilizer consumption potential, keeping in view the irrigated areas and areas receiving adequate rainfall. The requirements of each State for N,  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$  have been split into straight and mixed forms after taking into account the time of application of the fertilizers; and these requirements have also been grouped into four geographical zones (Table 2).

The types of fertilizers to be produced can be indicated only after knowing the cost of production of different kinds of fertilizer and the facilities available for their manufacture at various places. Since this information is not available, the targets of production of straight and complex fertilizers in terms of nitrogen and  $\text{P}_2\text{O}_5$  have been worked out, assuming that to produce 80 tonnes licensed capacity required will be 100 tonnes of the material.

**Phosphate:** Taking into consideration the above criterion, the production capacity of straight phosphatic fertilizers works out as 32,000, 58,000, 26,000 and 70,000 tonnes of  $\text{P}_2\text{O}_5$  in the North, West, East and South Zones respectively. Some portions of these will be used directly and the rest for preparing fertilizer mixtures.

**Complex:** In regard to the complex fertilizers, the quantities of nutrients in the different zones, worked out more or less on the basis of the recommendations by the different States, are as follows:

	N	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$
North	1,82,545 (2,28,180)	2,08,487 (2,60,610)	39,568 (49,460)
West	1,76,475 (2,20,595)	1,96,229 (2,45,285)	27,983 (34,980)
East	1,59,177 (1,98,970)	1,93,051 (2,41,315)	65,103 (81,380)
South	2,84,579 (3,55,725)	3,50,160 (4,37,700)	2,23,122 (2,78,905)
Total	8,02,776	9,47,927	3,55,776

[Figures in brackets indicate production capacity]

TABLE 1—FERTILIZER REQUIREMENT FOR FOURTH PLAN

Sl. No.	State	Cropped Area, million acres	Potential Requirements (M. Tons) Based on Fertilizer Recommendations			Estimated Requirements (M. Tons) During Fourth Plan		
			N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
1	2	3	4	5	6	7	8	9
1. Andhra Pradesh ..		37.29	2,79,559	1,71,299	1,18,716	2,32,478	1,29,146	79,457
2. Assam ..		6.21	71,282	64,338	34,370	33,804	20,041	8,424
3. Bihar ..		30.86	3,71,353	2,93,916	1,73,137	1,77,061	80,811	30,911
4. Gujarat ..		23.05	2,13,244	1,41,847	3,356	1,12,314	52,254	2,631
5. Kerala ..		6.64	85,439	61,183	71,077	65,619	46,014	49,864
6. Jammu & Kashmir ..		2.23	21,936	9,959	5,354	10,423	4,088	2,197
7. Madhya Pradesh ..		48.84	2,42,567	2,22,551	2,268	92,922	66,383	907
8. Madras ..		19.24	1,81,282	1,35,955	83,505	1,47,578	1,00,552	54,063
9. Maharashtra ..		48.92	4,25,063	1,76,325	34,959	2,38,484	91,542	24,446
10. Mysore ..		26.69	1,82,213	1,58,443	38,838	1,20,553	75,222	23,856
11. Orissa ..		17.23	1,81,808	1,19,689	22,074	79,855	35,344	6,672
12. Punjab ..		26.68	2,60,421	1,18,997	63,928	1,65,593	52,770	26,632
13. Rajasthan ..		41.95	3,28,746	1,55,264	30,763	1,06,485	32,867	5,934
14. Uttar Pradesh ..		68.98	6,17,471	3,59,850	13,973	3,23,285	1,42,313	4,192
15. West Bengal ..		17.17	1,39,881	1,09,981	15,607	86,852	49,008	7,350
16. Delhi ..		0.24	2,541	1,020	748	1,569	523	431
17. Himachal Pradesh ..		0.60	6,352	4,333	454	2,420	941	182
18. Tripura ..		0.59	6,215	4,946	4,900	2,177	1,507	953
19. Manipur ..		0.20	1,815	908	—	545	182	—
20. Plantations ..		1.36	42,481	19,908	24,700	42,481	19,908	24,700
TOTAL ..		425.00	36,61,669	23,30,712	7,42,727	20,42,498	10,01,416	3,53,802

TABLE 2—ZONE-WISE CONSUMPTION TARGETS DURING THE FOURTH PLAN

Figures in Metric Tonnes

Zone	State	Straight		Mixture			Total			
		N	P <sub>2</sub> O <sub>5</sub>	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	
North										
	Jammu & Kashmir	..	5,503	68	4,920	4,020	2,197	10,423	4,088	2,197
	Punjab	..	1,10,422	11,561	55,171	41,209	26,632	1,65,593	52,770	26,632
	Rajasthan	..	63,733	4,335	42,752	28,532	5,934	1,06,485	32,867	5,934
	Uttar Pradesh	..	1,88,937	8,970	1,34,448	1,33,343	4,192	2,23,285	1,42,313	4,192
	Delhi	..	885	27	684	496	431	1,569	523	431
	Himachal Pradesh	..	618	54	1,802	887	182	2,420	941	182
	TOTAL	..	3,70,098	25,015	2,39,677	2,08,487	39,568	6,09,775	2,33,502	39,568
West										
	Gujarat	..	40,278	558	72,036	51,696	2,631	1,12,314	52,254	2,631
	Madhya Pradesh	..	35,516	6,731	55,406	59,652	907	92,922	66,383	907
	Maharashtra	..	1,56,315	6,661	81,669	84,881	24,446	2,38,484	9,1542	24,446
	TOTAL	..	2,34,609	13,950	2,09,111	1,96,229	27,984	4,43,720	2,10,179	27,984

TABLE 2—Contd.

*East*

Assam	..	..	18,117	54	15,687	19,987	8,424	33,804	20,041	8,424
Bihar	..	..	1,01,180	2,568	75,881	78,243	30,911	1,77,061	80,811	30,911
Orissa	..	..	29,684	735	50,171	34,609	6,672	79,855	35,344	6,672
West Bengal	..	..	8,131	2,777	78,721	46,231	7,350	86,852	49,008	7,350
Manipur	..	..	—	—	545	182	—	545	182	—
Tripura	..	..	408	—	1,769	1,507	953	2,177	1,507	953
Tea	..	..	10,821	—	10,821	8,115	10,821	21,642	8,115	10,821

TOTAL	..	..	1,68,341	6,134	2,33,595	1,88,874	65,131	4,01,936	1,95,008	65,131
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*South*

Andhra Pradesh	..	..	1,31,156	7,514	1,01,322	1,21,632	79,457	2,32,478	1,29,146	79,457
Kerala	..	..	34,582	699	31,037	45,315	49,864	65,619	46,014	49,864
Madras	..	..	80,894	1,497	66,684	99,055	54,063	1,47,578	1,00,552	54,063
Mysore	..	..	40,480	3,630	80,073	71,592	23,856	1,20,553	75,222	23,856
Plantations	..	..	10,419	—	10,420	11,793	13,879	20,839	11,793	13,879

TOTAL	..	..	2,97,531	13,340	2,89,536	3,49,387	2,21,119	5,87,067	3,62,727	2,21,119
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## Grand Total—

N = 20,42,492

P<sub>2</sub>O<sub>5</sub> = 10,01,416K<sub>2</sub>O = 3,53,802

It has been suggested from cost consideration to produce granulated fertilizer mixtures in the same plants where the complex fertilizers are produced.

For the Third Plan, production of complex fertilizer with ratio 1 : 1 has already been licensed in the western and southern zones and the capacities licensed are 1,01,000 and 73,000 tonnes respectively. There is also a licensed capacity for the production of ammonium phosphate sulphate (16-20) in the southern zone, which in terms of plant nutrients is equivalent to about 39,000 and 49,000 tonnes of nitrogen and P<sub>2</sub>O<sub>5</sub> respectively. Besides, licensed capacity of 40,000 tonnes of nitrogen and P<sub>2</sub>O<sub>5</sub> in the west zone, 18,000 tonnes each of nitrogen and P<sub>2</sub>O<sub>5</sub> in the west zone, 18,000 tonnes each of nitrogen and P<sub>2</sub>O<sub>5</sub> in the east zone and 54,000 tonnes each of nitrogen and P<sub>2</sub>O<sub>5</sub> in the southern zone will be available from straight fertilizers viz. ammonium sulphate (existing or proposed), superphosphate (existing) for the preparation of fertilizer mixtures.

Therefore, during the Fourth Plan the extra requirements of fertilizer mixtures over the Third Plan production rate will be as follows: 2,28,180 and 2,60,610 tonnes

of nitrogen and P<sub>2</sub>O<sub>5</sub> respectively in the west zone; 1,80,970 and 2,23,315 tonnes in east zone, while potassic fertilizers will be imported and added according to requirements.

**Nitrogenous:** For preparing fertilizer mixture likely to be available from capacity already licensed during the Third Plan, 40,000, 18,000 and 54,000 tonnes of nitrogen as ammonium sulphate are needed for the west, east and south zones respectively. It has been suggested that the availability of 20,000, 80,000, 6,000 and 1,10,000 tonnes of nitrogen in the form of ammonium sulphate in the north, west, east and south zones respectively may be ensured during the Fourth Plan. There is already production capacity of 1,10,000 tonnes of nitrogen in the east zone, so after meeting the requirement of this zone a surplus of 1,02,000 tonnes nitrogen in the form of ammonium sulphate is available which might satisfy the ammonium sulphate requirements in the east and north zones and also a part of the west zone. In addition there is also licensed capacity of 42,000 tonnes nitrogen in the South, which could also meet a part of the requirement of ammonium sulphate in that

zone. In the north zone, after providing 2,28,000 tonnes nitrogen in mixed fertilizer and 20,000 in the form of ammonium sulphate there will be a deficit of 3,35,000 tonnes of nitrogen. In the west zone after producing 80,000 tonnes of nitrogen in mixed form and also after meeting a part of its ammonium sulphate requirements from the east zone there is need for the production of 58,000 tonnes of nitrogen as ammonium sulphate and 1,09,000 tonnes in some other suitable form.

The above analysis has indicated that 3,35,000, 1,09,000, 52,000 and 1,57,000 tonnes of nitrogen in the north, west, east and south zones in the form other than ammonium sulphate are required to be produced. The deficit of 3,35,000 tonnes of nitrogen in the north zone, 1,09,000 tonnes in the west, 52,000 tonnes in the south zone may be made good by the production of a high analysis nitrogenous fertilizer, like urea. A part may be met from ammonium chloride obtained as a by-product in soda ash industry.

In short, the types of fertilizers and their production capacity (extra) during the Fourth plan would be as follows:

TYPE OF FERTILIZER WITH CAPACITY, TONNES

Zone			N	P <sub>2</sub> O <sub>5</sub>
<i>North</i>				
Mixed Fertilizer	..	..	2,28,000	2,60,000
Urea & By-product Amm. Chloride*	..	..	3,35,000	—
Total	..	..	5,63,000	2,60,000
<i>West</i>				
Mixed Fertilizer	..	..	80,000	1,04,000
Amm. Sulphate	..	..	58,000	—
Urea & By-product Amm. Chloride*	..	..	1,09,000	—
Total	..	..	2,47,000	1,04,000
<i>East</i>				
Mixed Fertilizers	..	..	1,81,000	2,23,000
Urea	..	..	52,000	—
Total	..	..	2,33,000	2,23,000
<i>South</i>				
Mixed Fertilizer	..	..	1,90,000	2,62,000
Amm. Sulphate	..	..	68,000	—
Urea & By-product Amm. Chloride*	..	..	1,57,000	—
Total	..	..	4,15,000	2,62,000
Grand Total	..	..	14,58,000	8,49,000

\* The total quantity of by-product ammonium chloride in different zones will be 2,00,000 tonnes (50,000 te/N)

In a memorandum on "Fertilizers in the Fourth Plan" submitted to the Planning Commission, the Fertilizer Association of India, New Delhi, has presented an alternative method of estimating fertilizer requirements to produce additional quantities of foodgrains and other agricultural produce needed by the population in 1970-71. The present production of foodgrains is 79 m.tons, while by 1970-71 the population is estimated at 547.1 millions and the total cropped area expected to be 110 m.acres. Its estimates are based on two levels of nutrition viz. 16 and 17 oz. per capita (Table 3).

Taking into consideration the requirement of fertilizers for non-food crops the total fertilizer requirements in 1970-71 are as follows: (i) at the level of 16 oz/capita 3.44 m.tons and (ii) at 17 oz/capita 4.72 m.tons. By applying the ratio recom-

mended for India by agronomists which is 4N : P<sub>2</sub>O<sub>5</sub> : 1K<sub>2</sub>O, the requirements of plant nutrients should be as follows:

		N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
		(m. tons)		
At the level of—				
16 oz/capita	..	1.97	0.98	0.49
17 oz/capita	..	2.70	1.35	0.67

The consumption targets proposed by the Planning Commission correspond fairly closely with the 16 oz/capita in respect of N and P<sub>2</sub>O<sub>5</sub>, but is substantially lower in the case of K<sub>2</sub>O. From the point of view of nutrient balance potash has not received the consideration it should have. The proposed plant food ratio works out to 4N : 2P<sub>2</sub>O<sub>5</sub> : 0.7K<sub>2</sub>O, while in the Third Plan the target ratio was 5N : 2P<sub>2</sub>O<sub>5</sub> : 1K<sub>2</sub>O. In the opinion of FAI there should be a closer balance between N and K<sub>2</sub>O in the Fourth Plan and potash be raised to 0.5 m.tons. The Plan targets are about 30 per cent lower than the figures worked out on a 17 oz./capita basis.

From the standpoint of ample foodgrains supplies for improving the nutritional level of the people and building up buffer stocks it is desirable to adopt the higher targets corresponding to 17 oz./capita consumption rate, while those proposed by the Planning Commission viz. 2.0 N, 1.0 P<sub>2</sub>O<sub>5</sub> and 0.35 m.tons K<sub>2</sub>O may be prescribed as minimal and manda-

TABLE 3—FOODGRAIN & EQUIVALENT FERTILIZER REQUIREMENTS

IN 1970-71, M. TONS

Basis: 16 oz. Consumption/Capita; plus 12.5% for feed, seed & wastage			Basis: 17 oz. Consumption/Capita; plus 12.5% for feed, seed & wastage plus margin against natural calamities		
Total Quantity of Foodgrains Required	Additional Production over Present Level	Fertilizer Equivalent of Additional Production	Total Quantity of Foodgrains Required	Additional Production Over Present Level	Fertilizer Equivalent of the Additional Production
102.2	23.2	2.32*	115.0	36	3.6*

\*Assuming that 1 unit of plant food will produce 10 units of additional grain.

tory, which should be exceeded by as much as possible.

FAI has called for liberalization of the agricultural credit, expansion of soil testing and advisory services, ensuring adequate and timely supplies in a greatly expanded distribution network, educating and motivating the farmer and safeguarding the farmer's interests through crop insurance, etc. It has suggested for setting-up an autonomous Central Fertilizer Promotion Board with branches in the States, free inter-state movement of fertilizers, subsidy to reduce the farmer's price of fertilizers, feasibility of distributing fertilizers to farmers on a barter basis.

In regard to the supply of nitrogen and phosphorus from domestic production to meet the targetted consumption, production capacity should be established in a manner to balance the consumption by the end of the Fourth Plan. According to the Planning Commission, the total capacity of existing nitrogen plants and of those under erection is 1,067,550 tons of nitrogen, which leaves a balance of 1.133 m.tons to be planned. This gap has been proposed by the Planning Commission to be covered by production from 13 new projects and expansion at Nangal, the proposed capacities ranging from 50,000-100,000 tons nitrogen. Some of the new projects, each of 200,000 tons of nitrogen capacity, are proposed at Cochin, Madras, Barauni and Haldia, using partly naphtha or refinery gases as feed stock. According to FAI these plants should have ammonia as their primary marketable product and should be encouraged to sell a substantial part of their ammonia to secondary processors for

making complex fertilizers by ammoniating superphosphates, neutralizing sulphuric and phosphoric acids. There should be no rigid attitude in regard to the location or size of unit or the nature of the feedstock and, in fact the economics of each particular project should be the criteria for licensing it. Also, there should be no rigid specification for end-product pattern.

The memorandum has also dealt on the distribution of fertilizers for enabling the Indian agriculture to increase production.

#### **FCI Ltd. During 1963-64**

Sri B. C. Mukharji, Chairman & Managing Director, presented a creditworthy picture of the working results of the Fertilizer Corporation of India Ltd., for the year ended on March 31, 1964 at the Annual General Meeting held on September 30, 1964. The gross profit of Rs. 9.29 crores indicated an improvement of about Rs. 2.25 crores over the previous year's performance. While the provision for depreciation absorbed Rs. 4.95 crores and Rs. 63.71 lakhs were paid to the Government by way of interest on loan, the balance Rs. 3.70 crores amounted to as profit, which is about 8 per cent of the paid-up capital (Rs. 48.05 crores), has been appropriated to the reserves in order to cover the financial needs for completing the projects under construction. The profit was partly due to the increase in the output of Nangal unit and partly because of the retrospective revision of retention prices of the fertilizers.

For the third year in succession, the Nangal unit exceeded its production target—the production during the year under

report being 3,74,164 tonnes which is equivalent to 97 per cent of the rated capacity. Sindri's production was as follows: ammonium sulphate 3,07,107 tonnes, double salt 47,211 and urea 18,116.

Discussing the cost of manufacture at Sindri, the Chairman stated that the process of manufacture and the raw materials are the two basic causes for keeping it at a high level. The Nangal unit is based upon an expensive electrolytic process, the basic raw material for which, i.e. electric power, has increased in price, and this factor alone has upset the reduction in cost of production. Referring to the Namrup, Gorakhpur and Korba projects he said that it would not be wise to anticipate large profits from these units, as from the feasibility point of view they were just viable, and even if the operational efficiency of these units were improved the profits would be marginal. On the other hand, the Trombay unit, now nearing completion, and the Durgapur project held out promise for improved working results.

Dealing with the expansion plans of the fertilizer industry, Shri Mukharji said that the needs of the country for fertilizer were massive though the indigenous resources for fabricating production units were not sufficient. Even to import the minimum quantity of essential equipment for the expansion programme, a sizeable volume of foreign exchange was needed. He also said that the technical manpower in the planning and development division of the Corporation is capable of setting up two fertilizers plants a year provided the essential machinery is procured.

# News in Brief

## Fertilizer and Food Production

According to UNO's review for 1963, the present world food production could be multiplied three or four times by using more fertilizers together with improved agricultural methods. Farmers in developing countries should be encouraged to use more fertilizers, and there should be easily available credit, secure land tenure, adequate distribution of fertilizers and improved marketing of products. During the 15-year period 1945-60, world fertilizer use was increased by 280 per cent, while world crop land area increased by less than 20 per cent. Most of the increase occurred in a well-developed agriculture, and the fertilizer consumption was highest in Europe, N. America and Oceania (75 per cent of world's supply with 27 per cent of world's population):

[The State of Food & Agriculture 1963, U.N.O: Abstr. NPKS Abstrs, 30(1964), 6, 3]

## Granulation of Urea

Granules of urea are formed by passing heated, discrete quantities of urea at a temperature above its melting point into a body of denser liquid e.g. woods, metal and Lipouritz alloy, which is maintained at a lower temperature than that of the melting point of urea, and collecting the urea granules from an upper free surface of the denser liquid. Any metal on the surface of the granules is removed by treating the granules in a rotary screen, passing them through a highly concentrated solution of urea, and finally into a centrifuge.

[Brit. Pat. No. 932, 997; Abstr. NPKS Abstrs. 30 (1964), 6, 9]

## Calcium Ammonium Orthophosphate

Three new calcium orthophosphate— $\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  and dimorphs of  $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ —have been detected in experimental fertilizers and as products of reactions of fertilizers with soils. The crystallographic properties of the new salts were determined, and their fields of stability defined in an exploration of the system  $\text{CaO}-\text{NH}_3\text{HPO}_4-\text{H}_2\text{O}$  that covered the

pH range 4 to 10. The results help to explain the reactions that occur in the ammoniation of orthophosphate. When diammonium phosphate is the ammoniating agent, formation of apatite is avoided. Dicalcium phosphate and diammonium phosphate are not a stable salt pair; fertilizers containing these salts will cake by formation of  $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ .

[Agric. & Food. Chem., 12 (1964), 3 198-201; Abstr., NPKS Abstrs., 30 (1964), 6, 4]

## Kellogg Synthesis Gas Process

In a recent French patent on a steam-reforming process, M. W. Kellogg Inc. claim that this process allows synthesis gas pressure in excess of 400 psig i.e. up to 1000 psig. While cost of the reforming furnaces has not increased above the equivalent cost of furnaces that produce synthesis gas at 10 psig, this process produces anhydrous ammonia at below \$22.50 per ton of ammonia. Increasing synthesis gas pressure can reduce by as much as 25 per cent the compression costs in an ammonia plant although the cost of the reforming furnace is increased.

The key to the new Kellogg process is heating the primary reformer effluent gas prior to injection into the secondary reformer. The part of the reforming duty is thereby shifted from the high-cost primary reformer to the relatively low-cost secondary reformer.

The preheating of the feed to the secondary reformer increases the amount of heat available for its reactions and so allows an increase in the hydrocarbon content of the primary reformer effluent. The reformer tubes can then be operated at a lower temperature, while the primary reformer can operate at higher pressure because of higher tube metal strengths. According to Kellogg's new patent, the temperature to which the tubes in the primary reforming furnace are heated may be reduced to correspond to allowable maximum metal temperature as the pressure is increased.

The following conditions are necessary: primary reforming temperatures of 1350-

1500°F, a molecular steam-to-carbon ratio of 3:1 to 6.5:1 and 8-15 per cent methane in effluent from the primary reformer.

[Nitrogen, (1964), 29, 32]

## New Fertilizer

Mitsubishi Chemical Industries Ltd. of Japan has developed a new high-analysis fertilizer, which requires to be applied only once in a growing season. Its trade name is PCP-urea.

The new material is produced by reacting 150 butyl aldehyde with urea and then combining it with nitrogen, phosphate and potash.

[Nitrogen, (1964), 29, 38]

## Lurgi Gasification Process

In 1961 the National Coal Board and the Gas Council of U.K. had initiated a joint study of the Lurgi Process for the total gasification of coal, to establish the most economic application of this process using the cheapest method of enrichment. One of the design studies considered by the Study Group showed that with existing technology town gas could be produced from a Lurgi plant at  $8\frac{1}{2}$  d/therm or even a little cheaper, which was no more expensive than gas from imported methane.

Since the study was begun, processes based on light petroleum distillates have been developed which produce town gas more cheaply than processes based on either coal or methane. Nevertheless, Coal Board thinks that since a rise in the price of these distillates could materially affect the situation, and in view of the strategic implications of dependence on imported feedstocks, further research into the gasification of coal should be continued to find better processes.

[ECN, 6 (1964), 138, 8]

## Award for Nangal Unit

The Committee for presidential award for public sector industrial undertakings has decided to award a certificate of Honour (Parchment) to the Fertilizer Corporation of India (Nangal Unit) for

satisfactory performance during 1962-63.

A similar award was received by the Sindri Unit last year for satisfactory performance during 1961-62.

[Indian, Press Serv., 14 (1964), 68, 4]

### Fertilizer Consumption Per Unit Area

A study of the Statewise fertilizer consumption of N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O per unit area of cultivated land indicates that the highest consumption is in the South 5.73 lb/acre (or 6.42 Kg/hectare), next comes the eastern region (1.66 lb/acre) followed by the western (1.42 lb) and northern (1.39 lb). The all-India average of all fertilizers consumed amounts to 2.41 lb/acre (=2.71 Kg/hectare), while the consumption in Japan is about 240 lb (=270 Kg/hectare).

The consumption of nitrogen per acre of cultivable land is highest in Andhra (5.07 lb), followed by Madras (5.06), Kerala (3.25) and Punjab (2.31). Other States which consume more than a pound are Delhi, U. P., Mysore, W. Bengal, Bihar, Gujarat and Maharashtra.

The consumption of phosphoric acid per acre is in the following order: Andhra (1.50 lb), Madras (1.09), Kerala (0.76), W. Bengal (0.76), Gujarat and Maharashtra (0.57) and Mysore (0.49). In other States, the consumption is below 0.30 lb/acre.

Potash is consumed mostly in the South—the highest consumption (i.e. 4.30 lb/acre)—being in Kerala. In other areas the consumption is as follows: Madras (1.17 lb), W. Bengal (0.47), Mysore (0.39).

[Production & Consumption of Fertilizers—Annual Reviews, 1963-64 F.A.I. June 1964, 41-43]

### FACT Expansion

The State-owned Fertilizers & Chemicals, Travancore has taken up the Rs. 12 crores third stage expansion programme, which when completed will increase the end-products capacity of its Alwaye factory to 2,00,000 tons of ammonium sulphate, 1,35,000 tons of ammonium phosphate, 25,000 tons of ammonium chloride, 44,000 tons superphosphate and 3,50,000 tons of NPK mixtures. A notable achievement of FACT was the development of a process for the conversion of by-product gypsum into ammonium sulphate.

FACT, it appears, has been asked to plan for the setting up of two new factories,

one in Cochin and the other at Madras, during the Fourth Plan.

[Chem. Weekly, 9 (1964), 11, 21]

### Licensing Policy for Future Fertilizer Units

Government of India is understood to have tentatively formulated a policy for licensing new fertilizer factories, which shall have bigger capacities than the present. They will be located as far as possible in coastal towns or near oil refineries from which naphtha is obtained, with the idea of bringing down the prices to the level of current import prices as a first step and then to reduce them even further.

Although the normal capacity of a fertilizer factory in future will be 100,000 tons of nitrogen, the Government will not be averse to the setting up of factories with a capacity of 200,000 tons of nitrogen.

[Chem. Weekly, 9 (1964), 15, 18]

### Price of Fertilizers

The Union Ministry of Fertilizers and Chemicals has fixed the prices for different types of fertilizers produced at the Sindri and Nangal units for five years—1962-63 to 1966-67—as hereunder:

<i>Retention Price, Rs. per tonne</i>			
	1962-63	1963-64	1964-65 to 1966-67
Ammonium Sulphate	329*	330*	316
Double Salt	443*	440*	426
Urea	628*	620*	582
Calcium Ammonium Nitrate	305*	268*	256

\* These prices included excise duty.

It was further agreed that the above prices would apply also to other factories as follows: (i) FACT for ammonium sulphate from 1963-64 onwards, (ii) Calcium ammonium nitrate for Rourkela fertilizer plant, and (iii) Trombay Unit for Urea for the first year's production till costs on the basis of naphtha are established.

The existing pool issue price of calcium ammonium nitrate, fixed at Rs. 278.00 per metric tonne Gross f.o.r. works/ports/despatching station freight paid by the

Fertilizer Pool to rail-head destination by the shortest and cheapest route, will continue beyond August 31, 1964 for a further period of one year.

### ICI to Extend Catalyst Capacity

The Agricultural Division of the Imperial Chemical Industries Ltd. are to spend over £ 300,000 on the expansion of their production capacity for catalysts for the most part at Clitheroe, Lancashire and some at their Billingham works. The extensions at Clitheroe are to meet the demands for the catalysts made there, especially those used in the ICI steam-naphtha reforming process. The catalyst for making ammonia from synthesis gas produced by the reform process is produced at Billingham.

[Chem. Weekly, 9 (1964), 14, 23]

### Use of Fertilizers

A technical experts committee is to be appointed immediately to examine the existing arrangements for the use of marketing distribution and promotion of the use of fertilizers for agricultural purposes. Its object is to evolve a suitable distribution and promotional agency for fertilizers in the Fourth Plan period. This decision was taken at a meeting of the Agricultural Production Board held on August 5, 1964 at New Delhi under the chairmanship of the Union Minister for Food and Agriculture.

[The Statesman, 8.8.64]

### Durgapur Fertilizer Project

At a press conference at Calcutta on August 10, Shri B. C. Mukharji, Chairman and Managing Director of the Fertilizer Corporation of India Ltd., stated that the projected Durgapur fertilizer plant, due to be completed by 1967, will have a production capacity of 100,000 tons of nitrogen and 108,500 tons of phosphate. The complex product will be ammonium phosphate-sulphate. The establishment of this unit, estimated to cost about Rs. 29 crores, is expected to yield 25 per cent return on capital.

The projects of the FCI under implementation were Trombay (90,000 tons of nitrogen and 45,000 tons phosphates), Namrup (45,000 tons nitrogen), Korba (1 lakh tons nitrogen), Gorakhpur (80,000 tons nitrogen). The total production would be 3,15,000 tons of nitrogen and 45,000 tons of phosphate, and to this would be

added the Durgapur production capacity. The feasibility reports for setting up fertilizer factories at Haldia, Barauni, Udaipur, Kotah and Rihand are also complete and rough estimates have been prepared. Haldia would be supplementary to the Durgapur unit. Shri Mukharji also indicated that provisions might also be made for four more plants during the Fourth Plan with the expansion of the Nangal Plant, and that FCI would be reluctant to accept terms under which foreign firms would get a toe-hold in the country.

The scheduled date for the commissioning of Namrup unit had to be delayed by six months because the site had to be shifted. For the Korba unit (in M. P.), expected to be ready for production by the end of 1967, collaboration was mostly from Italy and Canada.

#### Phosphate Deposits in Laccadives

Extensive deposits of calcium carbonate and phosphates have been noticed in the Laccadive islands by the Indian Bureau of Mines. The calcium carbonate is of coral origin, and the phosphates in the form of guano are plentiful in the 10 unoccupied and 9 occupied islands of the group extending over 11 sq. miles.

[The Statesman, 4.9.64]

#### Phosphatic Fertilizers from Tars

An effective fertilizer has been produced by Prof. Guseinov of Baku, U.S.S.R., by mixing refinery waste with apatites or phosphorites in the proportion of 1.5 parts to 1 part respectively.

[NPKS Abstrs, 29 (1964), May 4;  
Abstr. P & D Div., FCI Ltd., Sept.  
1964, 1]

#### Nitrogen in Animal Foods

In a publication entitled 'Chemistry in Agriculture' by Semyon Volpkovich by the Academy of Sciences, U.S.S.R., it has been indicated that addition of urea to the food of a group of cows in the Ukraine increased milk yield by 8 to 10 tonnes and their weight by 500 kg.

[NPKS Abstrs, 29 (1964), April, 1]

#### New Type Ammonium Nitrate

Nitrogen Division of the Allied Chemical Corporation, New York, has developed a product, known as Gold—An Ammonium

Nitrate, with a higher density and a new improved coating. It is drier to stay well in storage, handling and use. The product is produced in uniform, shot-shaped pellets, golden in colour. Pelleting is carried out in a 175 ft high tower.

[NPKS Abstrs, 28 (1964), April, 1;  
Abstr. P & D Div., FCI Ltd., Sept.  
1964, 1]

#### Manurial Requirements of Ground Nut

Studies on the cultural and manurial requirement of ground nut, was carried at Kesarwa farm (Budaun, U. P.) by Pathak and Varma during 1958-59 to 1961-62 with T 28 variety with doses of 0, 20 and 40 lb of  $P_2O_5$  per acre with three dates of digging. The average results indicated that 20 lb N+20 lb  $P_2O_5$  gave the highest yield of 1423 lb/acre and the treatment 10 lb N+20 lb  $P_2O_5$  yielded 1408 lb/acre. The application of nitrogen alone did not prove beneficial. The latter dose mentioned above brought maximum profit of Rs. 20 per acre. The optimum time of digging was found to be 130 days after sowing which yielded the highest return of 4178 lb/acre.

[FAI Inf. Serv., 5 (1964), 18, 3]

#### Urea-Sulphur Fertilizer

Shell Oil Co., New York, has developed a novel fertilizer material with the object of supplying simultaneously nitrogen and sulphur to the soil. This product has considerable resistance to caking and combines at will with elemental sulphur and urea in desired proportions.

[NPKS Abstrs, 29 (1964), May, 5]

#### Preparation of Diammonium Phosphate

It is quite possible to allow phosphoric acid to react with ammonia in a saturator in order to form diammonium phosphate and cause the latter to crystallize in mother liquor in which the ratio of impurities to  $P_2O_5$  is higher than that existing usually in wet process phosphoric acid.

Accordingly, a method of preparing diammonium phosphate comprises neutralizing with ammonia in a saturator phosphoric acid prepared by the wet process, separating the resulting crystallized diammonium phosphate from the mother liquor, and directly recirculating to the saturator a fraction of mother liquor.

[Br. Pat. No. 954, 222; NPKS Abstrs,  
29 (1964), May, 4]

#### Fertilizer Treatment of Tea

Tea is a valuable crop in the Black Sea coast of Turkey. In an experiment by the Tea Research Station in Rize each experimental plot, which included 20 tea bushes, received 112.5 kg/ha N in the form either of ammonium sulphate or ammonium sulphate-nitrate, and two plots received in addition 150 kg of  $K_2O$  as potassium sulphate. Ammonium nitrate-sulphate showed itself as superior to ammonium sulphate and a combination with potash afforded a further marked increase in yield.

[NPKS Abstrs, 28 (1964), April, 6]

#### Indo-American Venture in Fertilizer Industry

A joint corporation on the basis of 50-50 partnership is envisaged between the Indian Government and the proposed American consortium in increasing fertilizer production in the Fourth Plan. At the conclusion of their discussions with the Union Government, Mr. Stephen Bechtel, and Gen. Lucius D. Clay of the American consortium elucidated the salient features of their proposal.

The total cost of producing one million tons of fertilizer would be around \$ 500 million, half of it being foreign exchange element. The paid-up capital of the corporation would be around \$ 125 million, out of which over \$ 60 million would come from the U.S. consortium. Concrete proposals would, however, be made after the feasibility study undertaken by the Corporation for location of raw materials and size of projects is completed. The plants would go into production within 2½ years, and maximum use would be made of indigenous machinery, services and technical skill.

[Chem. Weekly, 9 (1964), 20, 21]

#### Nitrogenous Fertilizers

At a meeting of the Planning Commission, attended by Shri C. Subramaniam, Union Minister for Food and Agriculture, and Shri O. V. Alagesan, Minister in the Ministry of Petroleum and Chemicals, it was decided to create a production capacity of nitrogenous fertilizers of about 2.2 million tons by the end of the Fourth Plan to ensure a growth rate of 5 per cent in agriculture. The backlog in the actual production of nitrogenous fertilizers in the current plan should be made up. The meeting decided that a committee should be appointed to go into

the various aspects of fertilizer distribution.

[Chem. Weekly, 9 (1964), 14, 6]

The Government of India has asked the Bechtel Corporation of U.S.A. to prepare a feasibility report for producing one million tons of nitrogenous fertilizer. This American firm was sponsoring a consortium of some American chemical firms for construction of fertilizer plants.

According to present indications, the Union Government proposes to give priority to the expansion of the existing units, which will mean not only expeditious results but comparatively less expenditure. At present there are 8 'committed' fertilizer projects viz. at Trombay, Alwaye, Ennore, Vishakhapatnam, Gorakhpur, Koyali and Mangalore. The eighth project will be established in Rajasthan.

The urea plant at Neyveli, the biggest of its kind in Asia, will go into production in Feb. 1966. Test runs are expected to start next month. Being set up in collaboration with Italian and W. German firms, this factory will produce 1,52,000 tons of urea per annum using 1,500 tons of lignite per day for gasification.

[Indian Press Serv., 14 (1964), 62, 1 & ibid 68, 3]

#### Import of Semi-processed Fertilizers

The Union Ministry of Petroleum and Chemicals is examining a scheme, under which India's import of fertilizers, which is about 2,00,000 tonnes annually at present, can be doubled without additional foreign exchange expenditure. This scheme envisages import of twice that quantity in half finished form for almost the same cost in foreign exchange. The material will be processed internally.

[FAI Inf. Serv., 6 (1964), 16, 9]

#### Fertilizer Distribution

The Union Ministry of Food and Agriculture proposes to set up a technical experts committee to evolve a suitable distribution and promotional agency for

distribution during the 4th Plan, after examining the existing arrangements for marketing, distribution and promotion of the use of fertilizers. [Chem. Weekly, 9 (1964), 14, 4-5]. This committee will also examine the question of pricing of fertilizers, role of co-operatives in their marketing and role of extension services in their promotion and popularization.

At a seminar on 'Fertilizer use in Maharashtra State' held on Aug 5, 1964 under the auspices of the Fertilizer Association of India, a strong plea for increased use of fertilizers and a more efficient system of distribution to increase food crops was made. Dr. V. G. Vaidya recommended the creation of a fertilizer pool in the State so that the Government might procure fertilizers in a big way to encourage balanced fertilization by regulating their distribution. To carry the fertilizers to the cultivators road transport facilities, in addition to rail transport, should be extended to them from buffer godowns and the additional cost of transport be met from the fertilizer pool. Credit and subsidy should be provided to cultivators.

[FAI Inf. Serv., 5 (1964), 16, 4-6]

#### Fertilizer Cess

A fertilizer cess of Rs. 10.00 per acre on all irrigated land has been suggested by Mr. P. P. Vaidyanathan, Adviser to the Planning Commission. To encourage an extensive use of fertilizers, their prices should be reduced by 30-40 per cent. But the subsidy would work out to be an enormous sum during the Fourth plan when the value of fertilizer distributed is worth Rs. 300 to 500 crores per annum. The proposed cess would fetch Rs. 90 crores annually.

[FAI Inf. Serv., 5 (1964), 20 5-6]

#### Piped Transport of Potash

Saskatchewan Government (Canada) is considering a permit to research and build a pipeline from Saskatoon and Regina to Chicago for the transport of potash. In this way the pipeline company expects to

move 2 million tons of muriate of potash as a slurry in a year from Saskatoon and Regina to Esterhazy in two 8-inch lines (229 and 148 miles respectively) from where the line would proceed to Chicago as a 10 inch diameter pipe (915 miles). There would be 17 pumping stations 80 miles apart provided with cathodic protection.

[Canad. Chem. Process, 48 (1964), 7, 47-48]

#### Nitrophosphate

Under an order called the Fertilizer (Control) Fourth Amendment Order 1964, the following entry in regard to the standard 20 Nitrophosphate (12 : 9 : 12) has been made after item 19 in the schedule to the Fertilizer (Control) Order 1957 by the Government of India: nitrogen (minimum) 12.90, citrate-soluble phosphate as  $P_2O_5$  (minimum) 12.90, water-soluble phosphate (minimum) 6.45, moisture (max.) 1.50 and calcium nitrate (max.) 2.5 per cent by weight.

#### By-product Ammonium Sulphate

Ishihara Sangyo Kaisha, K. K. of Japan, producer of titanium dioxide, is now producing 9,000 t.p.m. of ammonium sulphate as a by-product from its ammonia neutralization process for waste sulphuric acid arising during titanium dioxide production.

[Sulphur, (1962), No. 52, 34]

#### Gypsum in Gujarat

Fairly rich deposits of gypsum estimated at 6.7 million tons have been found in Kutch and Jamnagar.

[Res. & Indus., 9 (1964), 184]

#### Ammonia Pipeline

The next step in pipelining of materials other than oil and gas may be long-range movement of anhydrous ammonia. A major U.S. oil company is studying the idea of such a pipeline. It would be several hundred miles in length.

[Oil Commentary, 2 (1964), 6, 10]

# STATISTICS

TABLE 1—FORMS IN WHICH FERTILIZERS ARE CONSUMED IN INDIA

Kind of Fertilizers	Consumption (metric tonnes)				Percentage Increase from			
	1960-61	1961-62	1962-63	1963-64*	1960-61 to 1961-62	1961-62 to 1962-63	1962-63 to 1963-64	1960-61 to 1963-64
1	2	3	4	5	6	7	8	9
Ammonium sulphate .. ..	717,779 (63.8)	792,404 (53.2)	811,582 (51.1)	850,000 (39.8)	10.4	2.4	4.7	18.4
Calcium ammonium nitrate .. ..	113,717 (10.0)	238,166 (15.9)	290,257 (18.2)	500,000 (23.3)	109.4	21.9	72.3	339.7
Urea .. ..	77,987 (14.8)	155,634 (22.3)	167,948 (22.5)	285,000 (28.5)	99.6	7.9	69.7	265.4
Ammonium sulphate nitrate .. ..	81,674 (9.2)	80,063 (6.8)	59,628 (4.7)	56,000 (3.3)	-2.0	-25.5	-6.1	-31.4
Ammonium chloride .. ..	6,740 (0.7)	8,351 (0.7)	4,131 (0.3)	15,000 (0.8)	23.9	-50.5	263.1	122.6
Chilean natural nitrate of soda .. ..	14,650 (1.0)	8,403 (0.4)	12,560 (0.6)	10,000 (0.4)	-42.6	49.5	-20.4	-31.7
Ammonium Phosphate Sulphate	Gr. 16:20:0	5,847 (0.4)	10,282 (0.5)	12,164 (0.6)	40,000 (1.5)	75.9	18.3	228.8
	20:20:0	—	—	23,646 (1.4)	40,000 (1.8)	—	—	69.2
Nitro-phosphate .. ..	994 (0.1)	5,000 (0.2)	15,246 (0.6)	20,000 (0.6)	403.0	204.9	31.1	1,912.1
Total (N) .. ..	231,817 (100.0)	307,077 (100.0)	327,774 (100.0)	439,890 (100.0)	32.5	6.7	34.2	89.8
Superphosphate .. ..	328,163 (97.6)	380,490 (95.8)	512,691 (90.0)	700,000 (85.8)	15.9	34.7	36.5	113.3
Ammonium phosphate Sulphate	Gr. 16:20:0	5,847 (2.2)	10,282 (3.2)	12,164 (2.7)	40,000 (6.1)	75.9	18.3	228.8
	20:20:0	—	—	23,646 (5.2)	40,000 (6.1)	—	—	69.2
Nitro-phosphate .. ..	994 (0.2)	5,000 (1.0)	15,246 (2.1)	20,000 (2.0)	403.0	204.9	31.1	1,912.1
Total (P <sub>2</sub> O <sub>5</sub> ) .. ..	53,804 (100.0)	63,580 (100.0)	91,159 (100.0)	130,580 (100.0)	18.2	43.4	43.2	142.7
Muriate of potash .. ..	38,842 (78.8)	45,616 (89.9)	63,649 (95.6)	90,000 (95.6)	17.4	39.5	41.4	131.7
Sulphate of potash .. ..	12,555 (21.2)	6,146 (10.1)	3,502 (4.4)	5,000 (4.4)	-51.0	-43.0	42.8	160.2
Total (K <sub>2</sub> O) .. ..	29,583 (100.0)	30,443 (100.0)	39,940 (100.0)	56,500 (100.0)	2.9	31.2	41.5	91.0

Note: Figures in brackets denote the proportion of each kind of fertilizer to the total expressed in terms of plant food.  
\*Estimated.

[Production & Consumption of Fertilizers, Annual Rev., 1963-64  
(Fertilizer Asscn. of India, New Delhi), 1964, 24-25]

TABLE 2—PRODUCTION AND CONSUMPTION OF FERTILIZERS IN DIFFERENT REGIONS OF INDIA

(Metric Tonnes)

Regions	..	..	Nitrogen <sup>1</sup>		Phosphoric Acid (P <sub>2</sub> O <sub>5</sub> ) <sup>2</sup>		Potash (K <sub>2</sub> O) <sup>3</sup>	
			1962-63	1963-64*	1962-63	1963-64*	1962-63	1963-64*
<i>South</i>								
Production	..	..	9,085	20,522	44,708	55,280	—	—
Consumption	..	..	161,005	203,820	42,052	59,290	29,928	37,750
Production-Consumption		..	-151,920	-183,298	+2,656	-4,010	-29,928	-37,750
<i>West</i>								
Production	..	..	3,982	4,120	24,942	32,320	—	—
Consumption	..	..	56,885	84,790	23,948	34,090	4,386	9,500
Production-Consumption		..	-52,903	-80,670	+994	-1,770	-4,386	-9,500
<i>North</i>								
Production	..	..	68,100	80,625	7,198	14,400	—	—
Consumption	..	..	69,990	96,470	8,351	15,000	145	600
Production-Consumption		..	1,890	-15,845	-1,153	-600	-145	-600
<i>East</i>								
Production	..	..	113,027	134,008	11,453	19,840	—	—
Consumption	..	..	39,153	54,810	10,660	13,400	5,481	8,650
Production-Consumption		..	+73,874	+79,198	+793	+6,440	-5,481	-8,650
<i>India</i>								
Production	..	..	194,194	239,275	88,301	121,840	—	—
Consumption	..	..	327,774	439,890	91,159	130,580	39,940	56,500
Production-Consumption		..	-133,580	-200,615	-2,858	-8,740	-39,940	-56,500

\*Estimated

1. The regional totals do not tally with all-India totals, since a small quantity of fertilizer is used for industrial and demonstration purposes for which region-wise break-up is not available.
2. The all-India total included phosphoric acid utilized in mixtures by superphosphate manufacturers, whereas the regional totals do not include this.
3. A small quantity of potash is produced in India. This has not been taken into account here.

[Production & Consumption of Fertilizers, Annual Review, 1963-64  
(Fertilizer Assn. of India, New Delhi), 1964, 28-29]

TABLE 3—CONSUMPTION OF N, P<sub>2</sub>O<sub>5</sub> & K<sub>2</sub>O IN INDIA—STATEWISE (1963-64)

(Metric tonnes)

State	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
Andhra Pradesh	74,238	29,795	1,570
Assam	585	661	524
Bihar	16,617	6,958	3,186
Gujarat	16,780	13,452	1,105
Jammu & Kashmir	1,172	19	—
Kerala	11,690	3,298	9,919
Madhya Pradesh	8,369	4,435	52
Madras	47,078	10,960	11,631
Maharashtra	48,190	14,798	6,929
Mysore	25,287	10,068	7,238
Orissa	3,267	809	497
Punjab	45,098	2,784	47
Rajasthan	5,843	1,697	—
Uttar Pradesh	70,314	6,018	219
West Bengal	18,115	8,087	6,061
Delhi	165	47	—
Himachal Pradesh	838	567	—
Manipur	139	31	—
Tripura	21	—	—
Nagaland	—	5	—
Pondicherry	1,022	73	—
Goa	624	224	—
Andamans & Nicobar	—	6	—
Laccadives	—	—	—
Coffee Board	6,466	38 <sup>1</sup>	—
U.P.A.S.I.	6,538	—	—
Rubber Board	1,253	—	—
Tea (N.E. India)	13,828	—	—
Industrial Users	1,722	—	—
Sikkim	—	—	—
Nepal	34	39	—
Used in Mixtures	—	5,925 <sup>2</sup>	—
Wastages	24	184	—
Miscellaneous	556	9	—
	425,872	120,987	51,886 <sup>3</sup>

Note: Calculated on the basis of distribution figures.

<sup>1</sup> Represents the quantity despatched by the "Central Fertilizers Pool" in the form of complex fertilizer.

<sup>2</sup> Represents the quantity utilised by superphosphate manufacturers only.

<sup>3</sup> Included 2,908 metric tonnes K<sub>2</sub>O as sulphate of potash, the State-wise distribution figures for which are not available.

[FAI Inf. Serv., 5(1964), 21, 8-9]

TABLE 4—PROGRAMME OF FERTILIZER PRODUCTION IN INDIA DURING THIRD PLAN

<i>Name of Units</i>	<i>Raw Material</i>	<i>End Product</i>	<i>Production Capacity, Tonnes N/Year</i>
<b>I. Existing Units (Including Units Under Construction)</b>			
1. Mysore Chemicals and Fertilizers Ltd. Belagula, Mysore .. .. .	Electrolytic Hydrogen	Ammon. Sulph.	1,320
2. Fertilizers and Chemicals (Travancore) Ltd. Alwaye, Kerala .. .. .	Electrolytic Hydrogen and Naphtha	Ammon. Sulph. Ammon. Phos Ammon. Chloride	33,000 21,000 6,000
3. Fertilizer Corpn. of India, Unit at Sindri, Bihar	Coke and Coke Oven gases	Ammon. Sulph Ammon. Sulph. Nitrate Urea	70,000 36,000 11,000
4. Fertilizer Corpn. of India, Unit at Nangal, Punjab	Electrolytic Hydrogen	Cal. Ammon Nitrate	80,000
5. Sahu Chemicals Ltd. Varanasi, U.P. ..	Coke	Ammon. Chloride	10,000
6. Unit Hindustan Steel Ltd. at Rourkela, Orissa	Coke Oven gases	Cal. Ammon. Nitrate	1,20,000
7. East India Distilleries and Sugar factories Ltd. Ennore, Madras .. .. .	Naphtha	Ammon. Phos.	8,250
8. Neyveli Lignite Corpr., Neyveli, Madras (under construction) .. .. .	Lignite	Urea	70,000
9. Unit of the Fertilizer Corpn. of India at Trombay, Bombay (under construction) .. .. .	Refinery gases and Naphtha	Urea Nitro. Phos.	45,000 45,000
10. Unit of the Fertilizer Corpn. of India at Namrup, Nahorkatiya, Assam (under construction) ..	Natural gas	Ammon. Sulph. Urea	20,000 25,000
11. Unit of the Fertilizer Corpn. of India at Gorakhpur, U.P. (under construction) .. .. .	Naphtha	Urea	80,000
12. By-Products Ammonium Sulphate from Coke-Ovens	...	Ammon. Sulph.	20,000
		<b>TOTAL</b>	<b>7,01,570</b>
<b>II. Units Likely to be Established by 1967-68</b>			
1. Andhra Sugar Ltd. at Kothagudiam (Andhra Pradesh) .. .. .	Coal	Urea	66,000
2. Coromandal Fertilizers Ltd., Vishakhapatnam (Andhra Pradesh) .. .. .	Naphtha	Urea Ammon. Phos.	8,000 72,000
3. Gujarat State Fertilizers Ltd. Bajuwa, Near Baroda, (Gujarat State) .. .. .	...	Ammon. Phos. Urea	56,000 40,000
		<b>Total</b>	<b>2,42,000</b>
		<b>GRAND TOTAL (I &amp; II)</b>	<b>9,43,570</b>

[Kale, M. N., Chem. Weekly, Annual No., 9 (1964), 21, 59]

TABLE 5—FOOD SUPPLIES AVAILABLE FOR HUMAN CONSUMPTION IN SELECTED COUNTRIES, Kg/caput/year

	Period	Cereals <sup>1</sup>	Starchy roots <sup>2</sup>	Sugar <sup>3</sup>	Pulses and nuts <sup>4</sup>	Vegetables <sup>5</sup>	Meat <sup>6</sup>	Eggs <sup>7</sup>	Fish <sup>8</sup>	Milk <sup>9</sup>		Fats (fat content)
										Fat	Protein	
	1	2	3	4	5	6	7	8	9	10		11
<i>Western Europe</i>												
Austria	1954/55—1956/57	118	96	31	2	63	47	8	3	7	8	18
	1957/58—1959/60	114	92	34	3	65	52	10	3	7	8	18
	1962/63	101	80	37	3	53	62	12	3	7	7	18
Belgium-Luxembourg	1954/55—1956/57	100	150	28	4	65	53	14	7	4	6	22
	1957/58—1959/60	92	144	30	4	69	58	15	7	5	7	21
	1960/61	95	126	33	4	75	56	16	7	5	6	21
Denmark	1954/55—1956/57	90	131	48	5	62	63	8	14	8	8	26
	1957/58—1959/60	82	128	46	4	66	68	9	15	9	8	28
	1961/62	77	123	48	6	66	68	11	17	9	9	28
Finland	1954/55—1956/57	118	109	38	2	19	32	8	11	13	13	18
	1957/58—1959/60	114	98	40	2	21	32	6	11	12	12	18
	1960/61	110	113	39	2	17	32	8	11	12	12	19
France	1954/55—1956/57	111	130	26	6	132	69	10	6	5	6	17
	1957/58—1959/60	106	107	30	6	127	74	11	6	6	7	17
	1959/60	101	109	31	6	132	83	11	6	6	7	18
Germany, Federal Republic	1954/55—1956/57	96	157	28	4	45	48	10	7	6	7	25
	1957/58—1959/60	88	143	28	3	46	54	12	7	6	7	25
	1962/63	78	129	30	2	47	61	13	7	6	7	26
Greece	1954-56	158	39	10	14	99	17	4	7	4	4	17
	1957-59	167	43	12	14	116	22	6	8	5	5	13
	1960	163	36	13	14	118	23	6	8	5	5	18
Ireland	1954-56	128	155	42	2	61	55	16	4	8	10	20
	1957-59	117	142	44	3	63	58	16	4	8	10	20
	1961	107	140	49	3	64	65	16	4	8	9	19
Italy	1954/55—1956/57	145	48	16	9	96	20	8	5	4	4	14
	1957/58—1959/60	138	49	19	10	128	25	8	5	4	4	15
	1962/63	134	51	24	8	140	31	9	5	4	4	17
Netherlands	1954/55—1956/57	90	96	39	4	66	43	10	5	7	9	24
	1957/58—1959/60	85	91	40	4	66	44	12	4	8	9	25
	1962/63	83	96	42	3	69	50	12	5	8	9	30
Norway	1954/55—1956/57	95	105	39	4	34	37	8	20	12	9	26
	1957/58—1959/60	84	104	38	3	36	38	8	18	12	9	25
	1962-63	77	95	39	3	28	39	9	20	11	8	25
Portugal	1954-56	125	113	15	8	110	17	3	18	1	1	16
	1957-59	122	103	17	8	105	17	3	20	1	1	16
	1961	118	104	18	8	107	20	4	20	1	1	16

TABLE 5—Contd.

		1	2	3	4	5	6	7	8	9	10	11
Spain	1954/55—1956/57	117	113	13	16	102	14	5	10	2	3	16
	1957/58—1959/60	112	115	15	16	114	16	5	11	2	3	18
	1961/62	111	125	18	17	134	21	8	11	2	3	20
Sweden	1954/55—1956/57	76	102	42	3	25	50	11	18	10	9	21
	1957/58—1959/60	74	92	41	3	25	50	12	18	10	9	21
	1961/62	72	86	39	3	30	51	12	19	10	9	22
Switzerland	1954/55—1956/57	101	74	40	7	75	51	10	3	10	10	17
	1957/58—1958/59	97	73	39	8	76	56	10	3	10	10	19
	1961/62	95	67	42	9	77	61	10	4	10	9	19
United Kingdom	1954/55—1956/57	88	98	47	6	58	68	13	10	7	7	22
	1957/58—1959/60	84	95	49	6	60	71	15	10	7	7	22
	1961/62	81	97	48	5	59	76	15	9	8	7	23
Yugoslavia	1954-56	186	60	10	10	39	23	2	1	3	4	9
	1957-59	187	67	14	10	50	24	3	2	4	5	10
	1960	186	70	15	10	56	30	3	1	4	5	13
<i>North America</i>												
Canada	1954/55—1956/57	74	68	44	5	72	81	16	6	8	9	20
	1957/58—1959/60	70	66	44	5	77	78	17	7	8	9	19
	1961/62	70	69	45	5	73	78	16	8	8	9	19
United States	1954-56	69	49	41	7	98	92	21	5	9	9	21
	1957-59	67	48	42	7	96	92	20	5	9	9	21
	1961	66	47	42	7	97	96	19	5	8	9	21
<i>Latin America</i>												
Argentina	1954-56	105	83	34	3	49	108	7	-2	5	5	18
	1957-59	116	70	34	2	44	109	7	2	4	4	16
	1960	109	76	32	3	46	96	8	2	4	3	16
Brazil	1954-56	103	117	32	26	19	26	3	2	2	2	8
	1957-59	97	120	34	26	8	30	3	2	2	2	7
	1960	106	123	36	29	8	27	3	3	2	2	7
Chile	1954-56	137	76	31	8	67	31	4	9	3	3	7
	1957-59	127	79	23	8	72	33	3	11	3	4	10
	1960	129	67	26	9	70	32	3	11	3	3	10
Colombia	1956-58	61	84	51	9	13	41	3	1	2	2	6
Ecuador	1954-56	78	78	25	12	23	11	4	3	3	3	4
	1957-59	74	90	24	13	30	15	5	4	3	3	4
	1960	69	96	26	12	30	14	4	4	3	3	5
Mexico	1954-56	128	10	33	19	24	20	4	2	2	2	10
	1957-59	122	8	32	21	24	23	6	2	3	3	9
	1960	123	9	29	21	25	22	5	2	4	4	10
Paraguay	1957-59	84	229	15	15	36	48	1	—	3	2	4

TABLE 5—Contd.

	1	2	3	4	5	6	7	8	9	10	11	
Peru	1952	103	169	20	9	50	20	3	2	1	1	6
	1957-59	83	136	24	9	80	7	1	5	1	1	8
	1960	91	136	22	9	77	17	1	5	1	1	7
Surinam	1959	98	15	23	7	12	10	3	11	1	1	9
Uruguay	1954-56	99	61	33	2	37	109	7	1	6	6	17
	1957-59	92	65	32	2	48	111	7	1	6	6	21
	1960	99	49	27	1	47	96	7	1	8	7	18
Venezuela	1954-56	81	78	32	13	10	20	5	6	3	3	7
	1957-59	83	88	33	16	13	24	4	8	3	3	8
	1960	102	111	37	15	14	25	4	8	3	3	9
Far East												
Ceylon	1954-56	125	34	17	34	42	3	1	5	1	1	4
	1957-59	126	22	18	30	43	3	1	6	1	1	4
	1961	126	37	18	30	42	2	1	5	1	1	4
China: Taiwan	1954-56	148	68	9	9 <sup>10</sup>	58	17	2	10	—	—	3
	1957-59	156	69	9	10 <sup>10</sup>	60	13	2	11	—	—	4
	1961	165	53	9	12 <sup>10</sup>	57	16	2	13	—	—	5
India	1954/55—1956/57	126	11	14	24	16	1	—	1	3 <sup>11</sup>	2 <sup>11</sup>	3 <sup>12</sup>
	1957/58—1959/60	132	10	14	23	16	2	—	1	3 <sup>11</sup>	2 <sup>11</sup>	4 <sup>12</sup>
	1960-61	140	11	18	24	16	2	—	1	3 <sup>11</sup>	2 <sup>11</sup>	4 <sup>12</sup>
Japan	1954-56	151	63	12	16 <sup>13</sup>	68	3	3	23	—	—	3
	1957-59	153	66	13	17 <sup>13</sup>	75	5	4	25	1	1	3
	1961	149	56	16	17 <sup>13</sup>	85	6	7	29	1	1	5
Pakistan	1954/55—1956/57	150	—	14	8	18	4	—	2	3 <sup>11</sup>	2 <sup>11</sup>	4 <sup>12</sup>
	1957/58—1959/60	153	4	15	7	18	4	—	2	2 <sup>11</sup>	2 <sup>11</sup>	3 <sup>12</sup>
	1960-61	153	4	13	5	16	4	—	2	2 <sup>11</sup>	2 <sup>11</sup>	3 <sup>12</sup>
Philippines	1954-56	118	47	13	3	—	9	2	8	—	—	3
	1957-59	120	46	12	4	—	11	3	10	—	—	3
	1961	119	42	14	6	14	15	3	10	—	—	3
Near East												
Israel	1954/55—1956/57	140	47	25	8	116	21	15	8	5	5	16
	1957/58—1959/60	123	41	29	7	117	30	19	7	4	5	16
	1960-61	120	37	32	7	114	35	19	7	4	5	17
Jordan	1957-59	124	12	21	12	87	7	1	1	1	1	7
	1960	109	15	20	8	154	7	1	1	1	1	6
Syria	1957	162	10	11	11	59	12	1	1	1	4	6
Turkey	1954/55—1956/57	201	29	10	13	76	14	2	2	2	3	8
	1957/58—1959/60	200	40	9	14	78	13	2	2	3	3	8
	1960-61	223	39	17	13	105	14	2	3	4	4	8

TABLE 5—Contd.

		1	2	3	4	5	6	7	8	9	10	11
United Arab Republic	1954/55—1956/57	188	9	13	10	66	13	1	5	3 <sup>11</sup>	2 <sup>12</sup>	4 <sup>13</sup>
	1957/58—1959/60	184	9	12	10	80	13	1	5	3 <sup>11</sup>	2 <sup>12</sup>	5 <sup>13</sup>
	1960-61	182	13	10	12	87	12	1	5	3 <sup>11</sup>	2 <sup>12</sup>	5 <sup>13</sup>
<i>Africa</i>												
Libya	1959	115	17	28	7	80	10	2	1	2	2	8
Cyrenaica	1957	115	6	33	4	20	8	2	1	5	4	5
	1958	109	8	33	4	17	8	2	1	6	5	5
Mauritius	1955-56	131	17	39	11	28	6	—	6	1	1	9
	1957-59	131	16	37	11	29	5	1	6	1	2	10
	1961	126	12	38	12	28	6	2	5	2	2	12
Rhodesia & Nyasaland, Fed. of Southern Rhodesia	1951-53	184	12	13	14	26	30	1	2	1	1	2
	1953	201	10	12	16	26	29	1	2	1	1	2
South Africa	1954-56	149	14	39	4	38	43	3	8	3	3	6
	1957-59	145	17	45	4	37	44	3	7	3	3	6
	1959-60	138	21	39	5	35	43	3	11	3	3	11
<i>Oceania</i>												
Australia	1954/55—1956/57	93	46	52	4	61	112	10	4	7	6	16
	1957/58—1959/60	86	53	51	4	63	115	11	5	7	7	16
	1960-61	86	40	49	4	62	106	12	5	7	7	15
New Zealand	1954-56	86	52	43	3	73	105	14	7	11	10	19
	1957-59	86	57	42	3	69	106	15	7	11	10	20
	1961	87	61	43	4	74	108	18	7	11	11	20

<sup>1</sup> In terms of flour and milled rice. <sup>2</sup> Including sweet potatoes, cassava, and other starchy roots. <sup>3</sup> In terms of refined sugar; raw sugar included on the basis of its calorie content: excluding syrup and honey. <sup>4</sup> Shelled equivalent of nuts; including cocoa beans. <sup>5</sup> In terms of fresh equivalent but including also minor quantities of processed vegetables in terms of product weight. <sup>6</sup> Including poultry, offal, and game; expressed in terms of carcass weight, excluding slaughter fats. <sup>7</sup> Fresh egg equivalent. <sup>8</sup> Estimated edible weight. <sup>9</sup> Milk and milk products, excluding butter, expressed in terms of fat and proteins. <sup>10</sup> Including soyabean curd in terms of soyabeans. <sup>11</sup> Including milk for butter-making. <sup>12</sup> Excluding butter. <sup>13</sup> Including "miso" and "shoyu" (soyabean preparations) in terms of soyabeans.

[The State of Food & Agriculture, (F.A.O., Rome), 1963, 203-205]

TABLE 6—CALORIE AND PROTEIN CONTENT OF NATIONAL AVERAGE FOOD SUPPLIES IN SELECTED COUNTRIES, Caput/day

				Period	Calories	Total protein (g.)	Animal protein (g.)
				1	2	3	4
<i>Western Europe</i>							
Austria	..	..	..	1954/55—1956/57	2,900	85	42
				1957/58—1959/60	2,980	87	45
				1962/63	2,920	86	48
Belgium-Luxembourg	..	..	..	1954/55—1956/57	2,970	88	44
				1957/58—1959/60	2,910	88	47
				1960/61	2,870	86	44
Denmark	..	..	..	1954/55—1956/57	3,360	91	52
				1957/58—1959/60	3,390	93	57
				1961/62	3,370	93	58
Finland	..	..	..	1954/55—1956/57	3,160	98	55
				1957/58—1959/60	3,110	94	53
				1960/61	3,110	93	53
France	..	..	..	1954/55—1956/57	2,890	95	47
				1957/58—1959/60	2,940	98	52
				1959/60	2,990	99	53
Germany, Fed. Republic	..	..	..	1954/55—1956/57	2,990	79	43
				1957/58—1959/60	2,940	79	46
				1962/63	2,950	80	49
Greece	..	..	..	1954-56	2,720	87	23
				1957-59	2,950	94	27
				1960	2,930	95	28
Ireland	..	..	..	1954-56	3,540	99	54
				1957-59	3,480	95	55
				1961	3,440	91	55
Italy	..	..	..	1954/55—1956/57	2,550	74	23
				1957/58—1959/60	2,630	77	26
				1962/63	2,750	79	30
Netherlands	..	..	..	1954/55—1956/57	2,940	80	43
				1957/58—1959/60	2,950	79	44
				1962/63	3,020	81	46
Norway	..	..	..	1954/55—1956/57	3,160	89	50
				1957/58—1959/60	3,010	84	49
				1962/63	2,930	80	48
Portugal	..	..	..	1954-56	2,450	70	23
				1957-59	2,440	71	26
				1961	2,500	73	21
Spain	..	..	..	1954/55—1956/57	2,520	71	20
				1957/58—1959/60	2,590	71	20
				1961/62	2,790	76	22

TABLE 6—Contd.

				1	2	3	4
Sweden	..	..	1954/55—1956/57	2,980	84	53	
			1957/58—1959/60	2,930	81	52	
			1961/62	2,940	83	54	
Switzerland	..	..	1954/55—1956/57	3,130	93	52	
			1957/58—1958/59	3,120	90	51	
			1961/62	3,210	91	52	
United Kingdom	..	..	1954/55—1956/57	3, 60	86	50	
			1957/58—1959/60	3,280	86	51	
			1961/62	3,250	89	54	
Yugoslavia	..	..	1954-56	2,780	89	22	
			1957-59	2,920	96	26	
			1960	3,070	96	26	
<i>North America</i> *							
Canada	..	..	1954/55—1956/57	3,150	97	63	
			1957/58—1959/60	3,110	95	63	
			1961/62	3,100	94	63	
United States	..	..	1954-56	3,150	94	66	
			1957-59	3,100	94	63	
			1961	3,100	92	66	
<i>Latin America</i>							
Argentina	..	..	1954-56	3,070	97	58	
			1957-59	3,090	98	57	
			1960	2,930	83	50	
Brazil	..	..	1954-56	2,580	65	18	
			1957-59	2,540	61	19	
			1960	2,690	65	18	
Chile	..	..	1954-56	2,540	77	26	
			1957-59	2,440	80	29	
			1960	2,480	79	28	
Colombia	..	..	1956-58	2,200	48	23	
Ecuador	..	..	1954-56	2,170	52	13	
			1957-59	2,230	56	18	
			1960	2,110	53	23	
Mexico	..	..	1954-56	2,380	64	17	
			1957-59	2,400	67	20	
			1960	2,490	68	22	
Paraguay	..	..	1957-59	2,500	68	26	
Peru	..	..	1952	2,070	58	10	
			1957-59	1,970	49	12	
			1960	2,040	50	12	

TABLE 6—Contd.

				1	2	3	4
Surinam	..	..	..	1959	1,810	41	14
Uruguay	..	..	..	1954-56	2,960	96	62
				1957-59	3,020	95	62
				1960	2,900	93	60
Venezuela	..	..	..	1954-56	2,010	54	21
				1957-59	2,170	61	24
				1960	2,490	66	24
<i>Far East</i>							
Ceylon	..	..	..	1954-56	2,070	44	8
				1957-59	2,030	45	9
				1961	2,060	44	8
China: Taiwan	..	..	..	1954-56	2,210	53	13
				1957-59	2,330	57	14
				1961	2,400	60	16
India	..	..	..	1954/55—1956/57	1,840	49	6
				1957/58—1959/60	1,910	51	6
				1960-61	2,040	53	6
Japan	..	..	..	1954-56	2,100	64	15
				1957-59	2,230	68	18
				1961	2,290	70	22
Pakistan	..	..	..	1954/55—1956/57	1,990	46	8
				1957/58—1959/60	1,980	46	7
				1960-61	1,970	45	7
Philippines	..	..	..	1954-56	1,720	38	9
				1957-59	1,790	42	11
				1961	1,830	43	14
<i>Near East</i>							
Israel	..	..	..	1954/55—1956/57	2,870	88	31
				1957/58—1959/60	2,780	84	33
				1960-61	2,800	84	35
Jordan	..	..	..	1957-59	2,050	55	6
				1960	1,830	50	7
Syria	..	..	..	1957	2,330	78	17
Turkey	..	..	..	1954/55—1956/57	2,780	88	14
				1957/58—1959/60	2,820	90	15
				1960-61	3,100	98	16
United Arab Republic	..	..	..	1954/55—1956/57	2,570	75	13
				1957/58—1959/60	2,530	73	12
				1960-61	2,530	75	12

TABLE 6—Contd.

				1	2	3	4
<i>Africa</i>							
Libya	..	..	..	1959	2,180	53	10
Cyrenaica	..	..	..	1957	2,110	55	16
				1958	2,090	55	18
Mauritius	..	..	..	1955-56	2,290	47	10
				1957-59	2,270	46	11
				1961	2,330	48	13
Rhodesia-Nyasaland, Fed. of Southern Rhodesia	..	..	..	1951-53	2,450	75	16
				1953	2,630	81	16
South Africa	..	..	..	1954-56	2,620	75	31
				1957-59	2,550	74	32
				1959-60	2,660	74	30
<i>Oceania</i>							
Australia	..	..	..	1954/55—1956/57	3,230	91	59
				1957/58—1959/60	3,210	91	61
				1960-61	3,150	90	59
New Zealand	..	..	..	1954-56	3,400	103	70
				1957-59	3,430	105	72
				1961	3,510	109	74

[The State of Food &amp; Agriculture, (F.A.O., Rome), 1963, 206-20]







